
II.F.2 Photoelectrochemical Systems for H₂ Production

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Start Date: 2005

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

Accomplishments

- Quantified corrosion resistance of GaPN, showing 300 hours lifetime for 1 μm GaPN top-cell under simulated water-splitting conditions.
- New tandem cell design for PEC water-splitting based on a silicon bottom-cell and CuGaSe₂ top-cell.
- Growth of CuGaSe material via electrodeposition for incorporation of 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 multijunction structures for high efficiency.

Objectives

- Identify, synthesize, and characterize new semiconductor materials that have the possibility of meeting the criteria for a viable photoelectrochemical (PEC) hydrogen-producing device.
- Design and synthesize multi-junction devices for high efficiency water splitting.

Technical Barriers

This project addresses the following technical barriers from the Photoelectrochemical Hydrogen Production section (3.1.4.2.6) of the Hydrogen, Fuel Cells, and Infrastructure Technologies Program Multi-Year Research, Development, and Demonstration Plan (MYRDDP):

(AQ) Materials Durability

(AP) Materials Efficiency

(AS) Device Configuration Designs

Technical Targets

The 2010 technical targets from the Multi-Year Program Plan PEC hydrogen production goals are as follows:

- Bandgap of 2.3 eV
- 10% conversion efficiency
- 1,000-hour lifetime

Introduction

It is clear that solar energy must be efficiently, inexpensively, and directly converted to dispatchable fuels such as H₂. PEC water splitting represents a clean, efficient, energy conversion process for utilizing sunlight to effect the splitting of water. However, PEC materials still have many fundamental barriers that must be addressed before this technology can be commercialized into widespread practice. Much research effort has been applied to these systems, and conversion efficiencies greater than the 10% desired by the U.S. DOE have been achieved. However, these high efficiency systems remain too unstable to achieve the goal of 10 years of operation, and the stable systems remain at non-viable efficiencies. Clearly, a new set of more stable materials must be identified and studied.

The focus of this project will be to discover and characterize a material set that (i) splits water into hydrogen and oxygen spontaneously upon illumination, (ii) has a solar-to-hydrogen efficiency of at least 5% with a clear pathway to a 10% water splitting system, (iii) exhibits the possibility of 10 years stability under solar conditions, and (iv) can be adapted to low-cost, volume-manufacturing techniques.

Approach

Our approach towards materials research in this area is progressing on two fronts: 1) studying promising high-efficiency materials and looking for greater corrosion resistance and 2) developing new low-cost thin-film materials for application as corrosion-resistant coatings and as possible water-splitting systems. Currently, the highest efficiency systems have the shortest lifetimes and the lower efficiency systems have the longest lifetimes. The optimal system will likely be a compromise between efficiency and lifetime.

Results

This year we continued our study of group III nitrides (GaPN) and thin films of CuInGaSSe for use as PEC materials and performed some preliminary measurements on silicon nitride (SiN).

The group III nitride materials are of interest as possible high-efficiency corrosion-resistant PEC devices. Corrosion runs were analyzed to determine the role that nitrogen content and operating conditions and solution environment play in epilayer corrosion resistance. The various materials were operated for 24 hours as photocathodes in 3M sulfuric acid electrolyte with the surfactant Triton-X 100. The electrode was illuminated using a 150-Watt tungsten DC lamp run at 10 amps. The light was attenuated to AM 1.5, as measured with a GaPN reference cell, with a neutral density filter and an infrared water filter. Electrode surfaces were treated with 10 mC/cm² pulsed platinum electrodeposition prior to experiments. During durability assessment a galvanostat imposed a constant cathodic current density of 5 mA/cm² by applying a potential between the working and platinum black counter electrode (no reference was used). The unvarying current density resulted in an equivalent charge density being passed for each of the electrodes. It is assumed that corrosion is occurring by oxidation of the elements composing the electrode. The corrosion products were quantified using inductively coupled plasma-mass spectrometry (ICP-MS) analysis of the corrosion solutions. Generally, the nitrides had less gallium in solution than solutions from similarly treated GaP. The durability analysis solution for a GaInP₂/GaAs tandem electrode that passed equivalent charge contained ten times more gallium content than a solution from a typical nitride material, despite having a lower gallium ratio in the epilayer (GaInP₂ is a mixed group III). Changing specific variables in the durability analysis led to corrosion results that validated some predictions. The validations are rationalized from the results plotted in Figure 1. In Figure 1 the gallium concentration [Ga] is normalized to account for variation in surface area and solution volume and is plotted for the same sample compositions run under a variety of conditions.

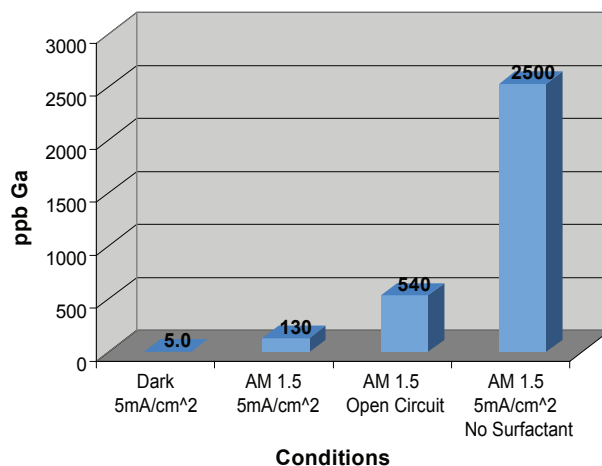


FIGURE 1. Ga Concentrations from ICP-MS Measurements from 24-hour Durability Solutions for a Variety of GaPN (2.1%N) Sample Conditions

The first observation is that illumination accelerates corrosion. This is evident in the high [Ga] from the illuminated electrodes relative to the dark sample. The explanation behind the dark vs. illumination material stability is that light promotes an electron from a bonding orbital to an anti-bonding orbital, leaving species at the interface prone to chemical attack and dissolution. Also, the presence of a hole in the surface bond means that one of the electrons in the bonding orbital has been removed leaving a positively charged surface species that can more easily react with the solution. In the absence of light, electrons are supplied through the bulk by a potentiostat, leaving bonds among surface species intact and thus more stable. Accordingly, anodic dissolution occurs on p-type in the dark and n-type in the light, which underscores the importance of conductivity type in curtailing corrosion. As solar energy conversion is the intended use of these materials, they will have to be able to persist in an illuminated environment.

The second observation concerns cathodic current flow offering protection from corrosion. The cathodic protection is evident from the low [Ga] in solutions from normal and dark runs compared to the sample that was illuminated but held at open circuit. This effect is likewise related to electron populations in the bonding orbitals. Under cathodic current flow, bonding orbital electrons in surface species are replenished by photoelectrons forced to the surface by the electric field in the depletion region. Open circuit condition does not force this movement of charges and thus restricts this mechanism of protecting the surface. Fortunately, in regard to current flow, the optimal conditions for hydrogen production also favor electrode stability.

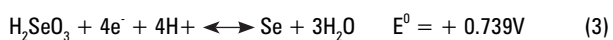
The final observation from ICP-MS data is that addition of surfactant to the electrolyte diminishes corrosion. Facile bubble evolution likely precludes problems associated with the adherence of hydrogen

gas to the semiconductor surface. Electron transfer to the solution is only possible where the surface is in contact with the solution. The aggregate constant current is maintained by increasing charge flow through the areas in contact with the electrolyte. It is assumed that the resulting large local variations in electron transfer rates contribute to surface instability. Bubble formation is also implicated in creating lenses that focus incoming radiation producing “hot spots.” The resulting non-uniform illumination causes local variations in surface potential, which may favor decomposition. The surfactant lowers the surface tension, and by reducing the bubble size preserves intimate contact at the semiconductor/electrolyte interface that is necessary to maintain efficiency and stability.

Thin-Film Materials: CIS-Based System

Large-area fabrication possibilities and low-cost material requirements combine to make thin-film materials a desirable materials option for PEC 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. CuGaSe_2 is a chalcopyrite semiconductor with a band gap near 1.7 eV. It is of interest as a top layer in a monolithic tandem device for PEC water splitting. Typically, CuGaSe_2 is deposited via high-temperature vapor deposition techniques. For our work, electrodeposition is studied as a low-temperature, low-cost route to the synthesis of CuGaSe_2 thin films.

Electrodeposition of CuInSe_2 and Cu(In,Ga)Se_2 thin films for photovoltaics has been reported, however the gallium content in these materials is low. Gallium incorporation has previously been shown to be difficult to obtain via electrodeposition due to its exceedingly negative reduction potential in aqueous solution. Thus, CuGaSe_2 has not been electrodeposited, due to the difficulty in obtaining adequate amounts of gallium in the film. Examining the reduction potentials of the components shown in Equations (1) to (3), it is seen that gallium has a very negative standard reduction potential (E^0) of -0.549 vs. normal hydrogen electrode (NHE), making electrodeposition a challenge.



Using aqueous metal-salt solutions, the effect of concentration, deposition potential, and substrate identity on the electrodeposition of gallium-containing thin films was studied. The early onset of the H_2

gas evolution reaction was found to contribute to poor film deposition and adhesion at large negative potentials. Hydrogen reduction was found to occur at a more positive potential on molybdenum electrodes than on indium-doped tin-oxide substrates. Film electrodeposition was performed on both Mo- and ITO-coated glass substrates. Table 1 presents the concentrations and deposition conditions for the films prepared in this study. Not all potentials were examined for electrodeposition on each substrate. This is due to the observed hydrogen gas formation during depositions at more negative potentials, which caused the films to delaminate or prevented deposition entirely.

TABLE 1. The composition of deposition baths investigated for the given electrodeposition potentials. The chosen substrates for those parameters are shown. Ratios are given normalized to $[\text{Cu}^{2+}] = 10 \text{ mM}$.

Cu:Ga:Se	-600 mV	-700 mV	-800 mV	-900 mV	-1000 mV	-1100 mV
1:10:0.5	Mo					
1:10:1	Mo					
1:10:1.5	Mo	Mo				
1:10:2	Mo	Mo	ITO	ITO	ITO	ITO

The electrodeposited films were analyzed by ICP-MS to determine the amount of Cu, Ga, and Se in the films. These values were converted to atomic percentages, shown in Table 2. Varying the Se/Cu

TABLE 2. Film compositions resulting from different bath compositions and applied potentials. Compositions were determined by ICP-MS analysis.

Cu:Ga:Se	-0.6 V	-0.7 V	-0.8 V	-0.9 V	-1.0 V	-1.1 V
1:10:0.5						
Cu (%)	41.86					
Ga (%)	32.68					
Se (%)	25.45					
1:10:1						
Cu (%)	33.18					
Ga (%)	30.71					
Se (%)	36.11					
1:10:1.5						
Cu (%)	39.03	32.06				
Ga (%)	1.76	21.73				
Se (%)	59.22	46.21				
1:10:2						
Cu (%)	37.14	33.32	33.69	31.85	35.47	27.00
Ga (%)	0.84	1.15	2.00	0.87	1.12	18.27
Se (%)	62.02	65.52	64.31	67.28	63.41	54.72

ratio in solution affected the overall film composition, with higher ratios suppressing gallium deposition until more negative potentials are reached. At lower H_2SeO_3 concentrations, potentials more negative than -0.6 V could not be used due to the large amount of hydrogen evolution. With more selenium in the solution, the production of hydrogen gas was suppressed at the electrode surface, and film deposition at more negative potentials could be achieved. In solutions with a higher H_2SeO_3 concentration, the formation of H_2Se prevented the evolution of H_2 gas bubbles at the surface, or at least decreased the quantity of evolved gas to enable the deposition of an adherent film.

Diffraction patterns of deposited films showed Cu_xSe_y phases present, and no peaks associated with gallium or Ga compounds were observed. However, thin films containing high gallium ratios were obtained and confirmed by ICP measurements, clearly indicating gallium incorporation was obtained in some of the electrodeposited films. This suggests that the gallium-containing phases are amorphous, or have a very small crystallite size. Annealing of these films may induce the growth of gallium-containing crystal phases and ultimately the desired stoichiometry for CuGaSe_2 .

Thin-Film SiN System

Currently, solid-state multijunction devices exist that can give the energy required for hydrogen production from water while accessing a large fraction of the solar spectrum. For example, commercially available triple-junction amorphous silicon (a-Si) devices can produce potentials greater than 1.6 V , which are sufficient for water-splitting. However, a problem with a-Si is its lack of stability when in solution; therefore, it requires a protective coating. Previous studies have shown that the use of amorphous silicon carbide as a protective coating offers some protection but at the same time absorbs too much light. A possible solution to this drawback is the use of silicon nitride, which can perhaps offer better transparency as well as the possibility of serving as a direct water-splitting material. With the ability to vary the composition of silicon nitride, and therefore the band gap of this material, the goal of this research is to offer a transparent protective coating for a-Si, realizing the U.S. DOE goal of 1,000 hours of stability as well as considering this material for driving the water-splitting reaction as a single-gap device.

Silicon nitride samples were prepared on indium tin oxide (ITO) glass at room temperature through DC magnetron sputtering at 200 W , with the addition of nitrogen at 4.5 mTorr , and varying of the argon introduction between 0 and 10.0 sccm . Photoresponse spectrum of the samples were taken, and it was determined that samples grown in pure nitrogen were

transparent and samples grown in the 4.8% N_2 showed an absorbance in the range of 500 to 600 nm , and initial absorbance measurements give a band-gap equal to 1.90 eV (Figure 2). X-ray diffraction measurements of the samples showed no peak shifts as compared to ITO, which was further supported by Raman analysis, indicating an amorphous material. Current-voltage (I-V) plots in $3\text{M H}_2\text{SO}_4$, with chopped light showed p-type behavior, as seen in Figure 3. This was unexpected as the open circuit potential indicated n-type behavior, leading to the conclusion that these samples are highly compensated.

Corrosion measurements revealed low currents and low noise, suggesting not only a stable material, but also a resistive material, and therefore viability as a transparent coating, assuming the conductivity can be increased. Future work at NREL will look at possible dopants to add to the material to enhance either the n-type or p-type behavior, as well as growing these materials on other substrates.

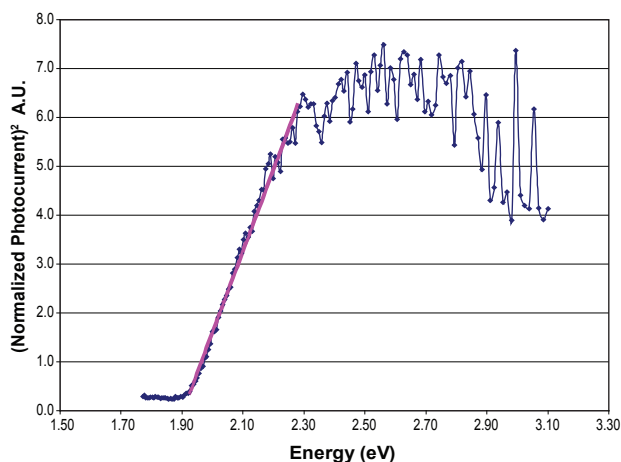


FIGURE 2. Analysis of SiN Photocurrent Showing 1.9 eV Bandgap

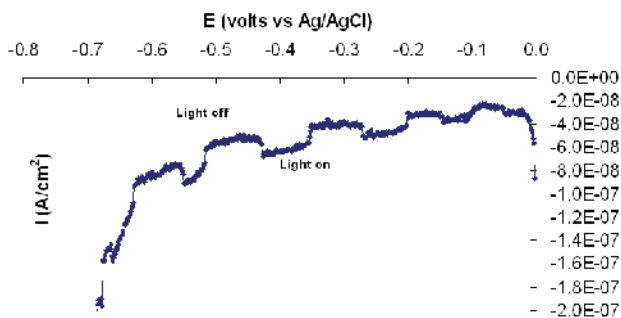


FIGURE 3. I-V Scan in $3\text{M H}_2\text{SO}_4$ of Sample Grown in 4.8% N_2 Obtained via Light Chopping

Conclusions

- Analysis of acid solutions where GaPN was tested under hydrogen evolution conditions confirmed exceptional stability in acid.
- Electrodeposition for CuGaSe₂ film formation showed modest success.
- Silicon nitride films were characterized. Preliminary data indicated that the material could be grown as a transparent film as well as with a bandgap of 1.9 eV.

FY 2006 Publications/Presentations

Papers

1. A. M. Fernández, N. Dhere, J. A. Turner, A. M. Martínez, L. G. Arriaga and U. Cano, "Photoelectrochemical Characterization of the Cu(In,Ga)S₂ Thin Film Prepared by Evaporation," *Solar Energy Materials and Solar Cells*, 85, Pages 251-259 (2005).
2. J. Turner, "The Sustainable Hydrogen Economy," *Geotimes*, August 2005.

Presentations

1. Presentation to high school and middle school science teachers (at NREL) on "The Sustainable Hydrogen Economy" as part of NREL Education Days.
2. Invited talk at Princeton University entitled "Material and Band Edge Engineering Approaches to Photoelectrochemical Water Splitting," Princeton, NJ.
3. Invited lecture at the CSIRO New Materials for Renewable Energy Frontier Science Workshop entitled "Photoelectrochemical Water Splitting: Materials and Systems," Melbourne, Australia.
4. Invited lecture at the University of New South Wales entitled "The Sustainable Hydrogen Economy," Sydney, Australia.
5. Scripps-Howard Fellows in Environmental Journalism (University of Colorado, Boulder) presentation entitled "Sustainable Hydrogen Economy."
6. University of Minnesota presentation entitled "Material and Band Edge Engineering Approaches to Photoelectrochemical Water Splitting."
7. Invited talk at the Air & Waste Management Association 97th Annual Conference entitled "The Sustainable Hydrogen Economy" in "Is the Hydrogen Economy Sustainable?" session.
8. Invited talk at the 2005 Colorado Renewable Energy Conference, presentation entitled "The Sustainable Hydrogen Economy."
9. Talk on hydrogen and fuel cells to middle and high school teachers as part of NREL's PPRISM Professional Development Day.

10. Invited talk at Fermilab (Chicago) entitled "The Sustainable Hydrogen Economy."
11. Presentation as part of the NREL 2005 Summer Intern Program, entitled "Hydrogen and Fuel Cells."
12. Kansas Energy Council, presentation entitled "Hydrogen Production and Fuel Cells."
13. Presentation to Institute of Nuclear Energy Research (Taiwan), entitled "Fuel Cell Research and H₂ from Photoelectrochemical Systems."
14. American Scientific Affiliation annual meeting, presentation entitled "Fuel Cell Technology and the Sustainable Hydrogen Economy."
15. Invited talk at the 2005 Solar World Congress entitled "The Sustainable Hydrogen Economy" at the "Renewable Fuels and Other Options to Reduce World Oil Consumption" forum.
16. Presentation to Fort Carson (Colorado) sustainability group, entitled "Hydrogen and Fuel Cells."
17. Denver Area Physics Teachers, presentation entitled "Fuel Cells and the Hydrogen Economy."
18. Department of Metallurgical and Materials Engineering, Colorado School of Mines, research seminar, presentation entitled "Photoelectrochemical Water Splitting: Materials and Systems."
19. Presentation to the University of Georgia's College of Agriculture and Environmental Sciences, the National Environmentally Sound Production Agriculture Laboratory, and representatives from the Georgia state government and Georgia agricultural industry, entitled "Sustainable Hydrogen."
20. Lecture for Colorado School of Mines fuel cell class, entitled "The Sustainable Hydrogen Economy."
21. "Photoelectrochemical Hydrogen Production," International Partnership for Hydrogen Energy, Renewable Hydrogen Workshop, Seville, Spain.
22. "Direct Photoelectrochemical Production of Hydrogen," Instituto de Ciencia de Materiales de Barcelona, Barcelona, Spain.
23. "Water Photolysis for the Production of Hydrogen," CeRMAE Energy Challenges, Barcelona, Spain.
24. "Photoelectrochemical Water Splitting: Materials and Systems," Department of Materials Science and Engineering, Rensselaer Polytechnic Institute.
25. Dr. Todd Deutsch, contributed talk, "Renewable Hydrogen: Direct Conversion of Photons to Fuel on III-V Nitrides," Pacifichem.
26. Dr. Jennifer Leisch, contributed talk, "CuGaSe₂/Si Tandem Devices for Photoelectrochemical Water Splitting," 208th Meeting of the Electrochemical Society, Los Angeles, CA, October 17, 2005.
27. Dr. Jennifer Leisch, educational outreach, presentation and demonstration on renewable energy, Pomona High School, Arvada, CO, February 1, 2006, organizing teacher: Robert Pizem, Earth Sciences Department.

- 28.** Dr. Jennifer Leisch, contributed talk, "CuGaSe₂/Si Tandem Electrodes for Photoelectrochemical Hydrogen Production," Western States Catalysis Club Symposium, Boulder, CO, February 24, 2006.
- 29.** Dr. Jennifer Leisch, contributed talk, "CuInSe₂ and Related Alloys for Photoelectrochemical Hydrogen Production," Department of Chemistry Seminar Series, Colorado School of Mines, February 28, 2006.
- 30.** Dr. Jennifer Leisch, keynote talk, "CuInSe₂ Materials for Photoelectrochemical Hydrogen Production," 1st Annual Symposium on Hydrogen from Renewable Sources and Refinery Applications, 231st Meeting of the American Chemical Society, Atlanta, GA, March 27, 2006.
- 31.** Dr. Jennifer Leisch, contributed talk, "CIS-Based Thin Films from Electrodeposited Precursors for Photoelectrochemical Hydrogen Production," 209th Meeting of the Electrochemical Society, Denver, CO, May 8, 2006.
- 32.** "Addressing the Challenges Ahead: The Sustainable Hydrogen Economy," Colorado Renewable Energy Society.
- 33.** "Hydrogen and Fuel Cell Technology," Connecticut Clean Energy Fund.
- 34.** "Addressing the Challenges Ahead: The Sustainable Hydrogen Economy," Schlumberger Carbon Services.
- 35.** "Photoelectrochemical Water Splitting: Materials and Systems," Department of Chemistry, University of Nevada, Las Vegas.
- 36.** "Materials and Systems for Photoelectrochemical Water Splitting," Department of Chemical & Metallurgical Engineering, University of Nevada, Reno.
- 37.** Dr. Todd Deutsch, contributed talk, "Photoelectrochemical Water Splitting on III-V Nitride/Si Tandem Semiconductor Materials," 209th Meeting of the Electrochemical Society, Denver, CO, May 8, 2006.