

II.D.2 Wide Bandgap Chalcopyrite Photoelectrodes for Direct Solar Water Splitting

Nicolas Gaillard

University of Hawaii / Hawaii Natural Energy Institute
2440 Campus Road, Box 368
Honolulu, HI 96822
Phone: (808) 956-2342
Email: ngaillar@hawaii.edu

DOE Manager: David Peterson

Phone: (240) 562-1747
Email: David.Peterson@ee.doe.gov

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- University of Nevada, Las Vegas, Las Vegas, NV
- Stanford University, Stanford, CA
- Lawrence Livermore National Laboratory, Livermore, CA
- National Renewable Energy Laboratory, Golden, CO

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Project End Date: September 30, 2018

- Demonstrate chalcopyrite-based PEC device with solar-to-hydrogen (STH) efficiency greater than 15%.

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
- (AJ) Synthesis and Manufacturing

Technical Targets

This project aims to develop efficient and durable PEC devices using low-cost semiconducting materials. Specifically, our project aims to modify the optoelectronic properties of the photovoltaic (PV)-grade copper chalcopyrite material class for PEC water splitting. Alongside, we are engineering new surface treatments to improve chalcopyrites' surface energetics, their catalysis toward hydrogen evolution reaction, as well as their resistance against photo-corrosion. The status of this project's technical targets is documented in Table 1.

TABLE 1. Progress towards This Project's Technical Targets for FY 2017

Task #	FY 2017 Milestones	Date	% Complete
1	Photocurrent density relevant to 16–17% STH conversion efficiency with a chalcopyrite 13–14 mA/cm ²	12/2016	92%
2	Fabricate Cu(In,Ga)S ₂ cells with Voc >900 mV	03/2017	88%
3	Durability >1,000 h at 8 mA/cm ² , with a stretch goal of 2,000 h	06/2017	33%
4	Hybrid photoelectrode PEC device with a standalone STH conversion efficiency of >15% generating at least 3 L H ₂ in 8 h	09/2017	

Overall Objectives

In line with the Fuel Cell Technologies Office Multi-Year Research, Development, and Demonstration Plan, our project aims to identify suitable semiconducting materials for efficient and durable photoelectrochemical (PEC) hydrogen production at a cost of \$2/kg or less. Specifically, our project aims to:

- Develop efficient copper chalcopyrite (Cu(In,Ga)(S,Se)₂) based materials with ideal optoelectronic properties for PEC water splitting.
- Identify appropriate surface treatments to prevent photo-corrosion, improve surface energetics, and enhance hydrogen evolution reaction.
- Demonstrate three liters of hydrogen produced in eight hours using a copper chalcopyrite-based standalone PEC device.

Fiscal Year (FY) 2017 Objectives

- Demonstrate copper chalcopyrite/buffer junction with open circuit voltage (Voc) over 900 mV.
- Improve chalcopyrite stability in aqueous electrolytes using MoS₂ as protection layers, with a durability goal of 1,000 hours continuous operation at 8 mA/cm².

FY 2017 Accomplishments

Accomplishments during the current project period include:

- Successful modeling of new selenide-based wide bandgap chalcopyrite candidates

- Characterization of the CuInGaS₂/CdS interface with spectroscopic techniques
- Voc over 850 mV achieved with 1.8 eV CuGa₃Se₃/CdS heterojunctions
- Photo-current density over 12 mA/cm² obtained with 1.8 eV CuInGaS₂
- Extended durability of CuGaSe₂ with MoS₂ protective coating, from 250 h to 350 h



INTRODUCTION

The goals of this project are to demonstrate PEC hydrogen production with a dual absorber system capable of generating at least three liters of hydrogen in eight hours and to develop a standalone system with STH conversion efficiency of 15% and operational life up to 2,000 hours.

APPROACH

The chalcopyrite material class, typically identified by its most popular PV-grade alloy, CuInGaSe₂, provides exceptionally good candidates for PEC water splitting. A key asset of this bandgap tunable, direct absorber, thin film semiconductor material is the outstanding photon-to-electron conversion efficiency, as demonstrated with CuInGaSe₂-based PV cells. An STH efficiency of 4% was achieved by our team in 2012 using a 1.6 eV bandgap CuGaSe₂ photocathode connected in series with three a-Si PV drivers (side-by-side architecture). The use of such coplanar architecture was dictated by the bandgap of CuGaSe₂, which was too narrow for a “stacked” multi-junction integration. With wide bandgap chalcopyrites, we will be able to stack the PEC device over the PV driver and increase the STH efficiency.

RESULTS

Task 1. PV-grade wide bandgap absorbers: theoretical modeling. This year we continued to investigate the properties of candidate chalcopyrite alloys, focusing on the optical properties and the electronic structure as a function of composition, as well as investigations into the influence of common impurities like H. Our studies identified that H impurities can have important implications on limiting the p-type dopability of several chalcopyrite compounds, particularly those incorporating Ag. Additionally, we identified that the B-containing CuBS₂ and CuBSe₂ compounds exhibit smaller fundamental bandgaps than previously assumed from experimental measurements of the optical bandgaps, which are reported to be 3.61 and 3.13 eV, respectively. Our results on the optical spectra of these

compounds identified a very weak absorption onset and that the fundamental bandgaps are actually much smaller than the optical gaps by roughly 0.8 eV. Our findings suggest that B incorporation into CuInS₂ or CuInSe₂ leads to conduction band edges that are much closer to those of the Ga-containing analogs than previously assumed.

Task 1. PV-grade wide bandgap absorbers: synthesis.

During this reporting period, CuInGaS₂ absorbers with a current density of 12 mA/cm² at –1 V bias were synthesized. The absorbers were made on molybdenum substrates by co-evaporating Cu, In, and Ga to form a Cu-rich metal alloy film with a Cu/(Ga+In) ratio of 1.3 and a Ga/(Ga+In) ratio of 0.32. The alloys were sulfurized by heating them with 150 mg S in a N₂-filled capsule at 600°C for 30 minutes. The absorbers were etched in 1 M potassium cyanide solution for three minutes to remove any Cu-S compounds formed, resulting in a Cu/Ga+In ratio of 0.93. These absorbers were then completed into PV devices with a chemical-bath-deposited CdS buffer layer, radio frequency magnetron sputtered ZnO (200 nm) window layer, and indium tin oxide (500 nm, with mask) top contact. The final device area was 0.12 cm². The quantum efficiency (QE) measurement of the best device at –1 V bias is shown in Figure 1, demonstrating 12 mA/cm² current density. The bandgap determined from the derivative of the QE cut-off is 1.8 eV. Future experiments with alkali treatments and reduced Cu excess in the metal alloy will be attempted to improve current density.

Task 2. Sub-surface energetics improvement: synthesis. We have continued material optimization to improve the properties of wide bandgap defect chalcopyrite

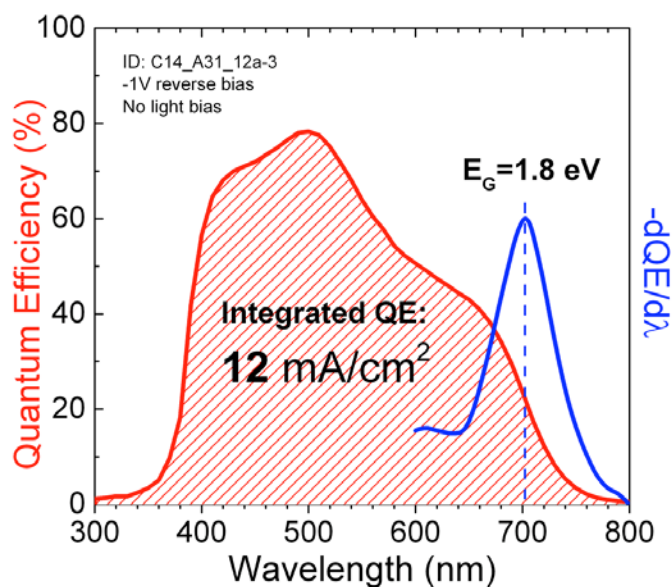


FIGURE 1. QE of best-performing CuInGaS₂ film made from sulfurizing a CuInGa alloy (red), and the bandgap determined from the derivative of the QE spectrum (blue)

CuGa₃Se₅ to achieve higher open-circuit voltage and photocurrent density. Several optimization strategies have been applied in recent material growth, including the control of sample growth temperature, bulk composition, film thickness, composition gradient, and alkaline post deposition treatments. A few device treatment strategies have also been tested to show improvement on device performance. Our results are primarily based on recent sample growth with increased growth temperature from the standard 550°C to 620°C. In general, we found that increasing the growth temperature to 620°C improves device characteristics, especially for the higher Voc. We now can regularly obtain 800–850 mV Voc using absorbers with about 1.8 eV bandgap (Eg). This is a significant accomplishment for the wide bandgap CuGa₃Se₅ material development, since a large voltage loss (Eg/q–Voc) represents a key energy loss associated with wide bandgap absorbers in general. For recent studies, the Cu/Ga ratio has been narrowed to about 0.33±0.03 in order to have the proper bandgap values (1.7 eV to 1.9 eV). Through our research we found that i) CuGa₃Se₅ may be too resistive, so thinner layers are desirable; ii) higher growth temperature works better; and iii) doping with NaF improves the fill factor of the devices.

Task 2. Sub-surface energetics improvement:

advanced characterization. This project year, University of Nevada, Las Vegas's work centered on X-ray photoelectron spectroscopy (XPS) measurements and analysis of the third sample set received from the University of Hawaii, as well as first ultraviolet photoelectron spectroscopy and inverse photoemission spectroscopy measurements. Furthermore, X-ray emission spectroscopy of various samples (including those discussed below) was performed at the Advanced Light Source (Berkeley Lab). The goal of these experiments is, in particular, to determine the electronic surface and interface structure of a sample series consisting of Cu(In,Ga)S₂ (CIGS) absorbers with CdS buffer layers of varying thickness (deposited using chemical bath deposition). The experimental results provide valuable information about the CdS/CIGS interface, including the band alignment of the valence and conduction band, as well as the electronic surface bandgaps. Figure 2 shows the XPS survey spectra of a (sulfurized) CIGS absorber and CdS/CIGS samples with increasing buffer layer thickness. The increase in chemical bath deposition time leads to an increase in Cd intensity, in parallel to a continual attenuation of absorber-related peaks (as expected). Because the CIGS-related Cu, In, and Ga signals are still detected for the intermediate buffer layer thickness, this sample is currently being investigated to monitor the interface-induced changes in surface band bending, to be combined with the results for valence band maximum and conduction band minimum obtained with ultraviolet photoelectron spectroscopy and inverse photoemission spectroscopy, respectively. The next project steps include an ion treatment series, necessary to remove surface adsorbates for a more accurate band edge determination, followed by

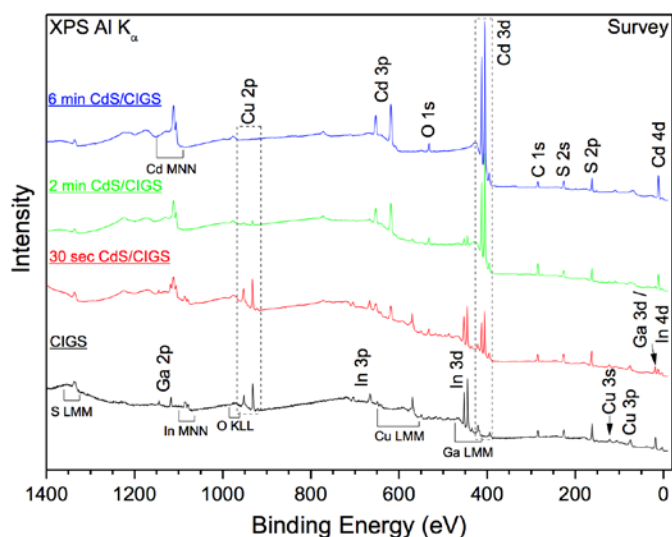
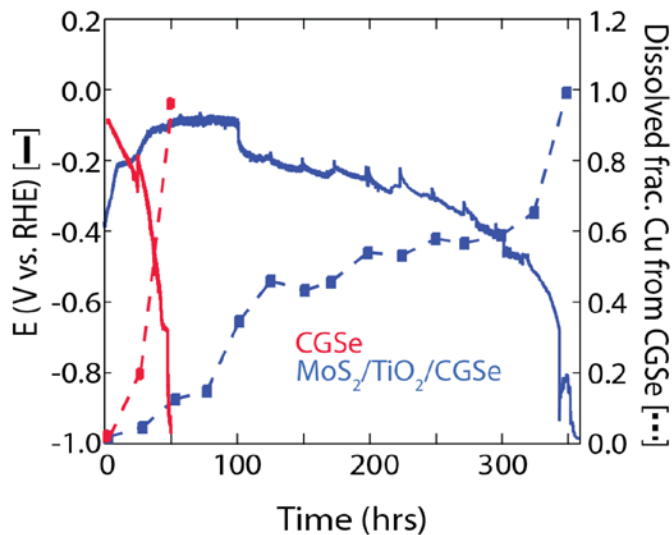


FIGURE 2. Al K_α XPS survey spectra of a Cu(In,Ga)S₂ absorber (“CIGS”) and three additional CdS/CIGS samples with increasing buffer layer thickness (deposition times of 30 seconds, 2 minutes, and 6 minutes, respectively)



RHE – reversible hydrogen electrode

FIGURE 3. Chronopotentiometry plot of CGSe electrodes with and without catalytic and protecting schemes. On the secondary ordinate, data from inductively coupled plasma are shown, demonstrating the fraction of Cu in the film that has dissolved into the electrolyte, sampled at intervals by aliquoting.

successive XPS, ultraviolet photoelectron spectroscopy, and inverse photoemission spectroscopy measurements.

Task 3. Surface catalysis and corrosion resistance.

During the third year of our project, we worked to develop conformal MoS₂/TiO₂ coatings to protect copper gallium selenide (CGSe) electrodes and buried-junction CdS/CGSe electrodes from corrosion in sulfuric acid electrolyte

during PEC hydrogen evolution. Figure 3 shows the results of our surface protection schemes and includes durability measurements for bare CGSe electrodes and CGSe electrodes with 7.5 nm of atomic layer deposition (ALD)-deposited TiO_2 and 4.5 nm of ALD-deposited MoO_x that has been converted to MoS_2 . All samples were tested by measuring the voltage required to obtain a constant current density of -8 mA cm^{-2} . The protected sample operates continuously for much longer than the bare CGSe sample, with the two electrodes failing at 350 h and 50 h, respectively. Overlaid in this figure is the fraction of the Cu atoms in the film that have dissolved into the acid electrolyte over the course of the measurement, as quantified at intervals by inductively coupled plasma analysis. The MoS_2 protecting scheme appears to provide enhanced durability to the CGSe film by slowing the rate of dissolution into the electrolyte.

CONCLUSIONS AND UPCOMING ACTIVITIES

- Achievement: Over 12 mA/cm^2 and 850 mV achieved with wide bandgap chalcopyrites. Durability improved with MoS_2 protective coating, from 250 h to 350 h.
- Achievement: Advanced modeling and characterization successfully integrated to accelerate materials and interface engineering.
- Future work: Finalize our study on CuGaSSe and CuInGaSSe to conclude on the effect of ordered vacancy compounds and re-focus effort on best candidates for final tandem PEC structure: Cu-poor CuGaSe_2 and CuGa_3Se_5 .
- Future work: Continue to develop ex situ and in situ spectroscopic techniques to better understand degradation mechanisms and evaluate SiO_2 passivation layer as an alternative to TiO_2 to meet the 1,000+ h durability goal.
- Future work: Validate tandem structure using CGSe, temperature-resistant transparent conductive oxide (Mo:InO_2), and silicon or GaAs model PV drivers, and benchmark STH efficiency of best-performing tandem device.

FY 2017 PUBLICATIONS/PRESENTATIONS

1. *Novel Chalcopyrite Materials for Economical Photoelectrochemical Hydrogen Production*. N. Gaillard, A.D. DeAngelis, and K. Horsley, the 231st Electrochemical Society Meeting, Symposium I03, 1532, New Orleans (LA), 2017.
2. *First-Principle Simulations in Chalcopyrite Based Photoelectrode Development*. T. Ogitsu, J. Varley, N. Gaillard, C. Heske, and M. Blum, the 231st Electrochemical Society Meeting, Symposium I03, 1529, New Orleans (LA), 2017.
3. *Development of Wide Bandgap Copper Chalcopyrite Materials for Economical Photoelectrochemical Hydrogen Production*. N. Gaillard, A.D. DeAngelis, and K. Horsley, the 230th Electrochemical Society Meeting, Symposium L04, 3630, Honolulu (HI), 2016.
4. *Photoelectrochemical and Solid-State Properties of Wide Bandgap Copper Chalcopyrites for Renewable Hydrogen Generation*. N. Gaillard, K. Horsley, and A. DeAngelis, the Materials Research Society Spring Meeting, Symposium ES7, ES7.16.02, Phoenix (AZ), 2017.
5. *Soft X-ray Spectroscopic Investigation of the CdS/Cu(In,Ga)S_2 Interface in Thin Films for Photoelectrochemical Water Splitting*. J. Carter, B. Elizan, M. Blum, K. Horsley, A. DeAngelis, W. Yang, L. Weinhardt, N. Gaillard, and C. Heske, the Materials Research Society Spring Meeting, Symposium ES7, ES7.4.04, Phoenix (AZ), 2017.
5. *Non-Precious Metal-Catalyzed Photoelectrodes for Hydrogen Production Via Solar Water Splitting*. T.R. Hellstern, A.D. DeAngelis, L.A. King, P. Chakthranont, R.J. Britto, N. Gaillard, and T.F. Jaramillo, the 230th Electrochemical Society Meeting, Symposium L04, 3718, Honolulu (HI), 2016.
6. *Solid-State Characterization of Wide-Bandgap CuGa(S,Se)_2 for PEC Water Splitting*. A.D. DeAngelis, K. Horsley, and N. Gaillard, the 230th Electrochemical Society Meeting, Symposium L04, 3714, Honolulu (HI), 2016.