II.C.5 Wide Bandgap Chalcopyrite Photoelectrodes for Direct Water Splitting

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Project End Date: September 30, 2017

Overall Objectives

In line with the Fuel Cell Technologies Office (FCTO) Multi-Year Research, Development, and Demonstration (MYRDD) 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 program 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 photocorrosion, improve surface energetics and enhance hydrogen evolution reaction.
- Demonstrate 3 L of hydrogen produced in 8 hours using a copper chalcopyrite-based standalone PEC device.

Fiscal Year (FY) 2015 Objectives

- Identify photovoltaic (PV)-grade chalcopyrite alloys with controlled energetics and microstructure
- Model energetics at the absorber/"buffer" p-n junction interface
- Evaluate dichalcogenides (e.g., MoS_2 and WS_2) as both corrosion protective layer and hydrogen evolution reaction (HER) catalyst

Technical Barriers

This project addresses the following technical barriers from the Hydrogen Production section of the FCTO MYRDD plan:

(AE) Materials Efficiency

(AF) Materials Durability

(AG) Integrated Device Configuration

(AJ) Synthesis and Manufacturing

Technical Targets

This project aims to develop efficient and durable PEC devices using low cost semiconducting materials. Specifically, our program aims to modify the optoelectronic properties of the 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 HER as well as their resistance against photo-corrosion. The status of the UH's technical targets is documented in Table 1.

FY 2015 Accomplishments

Accomplishments during the current project period include:

- Successful synthesis of bandgap tunable $Cu(In,Ga)S_2$ and $CuGa(S,Se)_2$ thin films.
- Modeling of interface energetics formed by CdS or ZnS with various chalcopyrites.
- Improvement of $CuGaSe_2$ photoelectrodes durability using MoS_2 as a protective coating.
- Proof-of-principle experiments for in situ studies of the chalcopyrites/electrolyte interface.

INTRODUCTION

The goals of this project are to (1) demonstrate PEC hydrogen production with a dual absorber system capable of generating at least 3 L of hydrogen in 8 hours and (2) to develop a standalone system with a solar-to-hydrogen (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 $CuInGaSe_2$, provides

TABLE 1. Progress towards Meeting Technical Targets for Photoelectrochemical Hydrogen Production

Characteristics	Unit	2015 / Ultimate Targets	UH project status
Solar-to-Hydrogen Energy Conversion Ratio	%	15 / 25	4[a] to 10[b]
Capital Cost of Concentrator & PEC Receiver	$/m^2	200 / 63	270[c]
Photoelectrochemical Hydrogen Cost	$/kg	17.30 / 2.10	13.2[d]
Annual Electrode Cost per TPD H_2	$/yr-TPD H_2	2,000,000 / 14,000	1,500,000[d]
1-Sun Hydrogen Production Rate	kg/s per m^2	1.2 x 10^{-6} / 2.0 x 10^{-6}	3 x 10^{-7} to 1 x 10^{-6}

[(a)] achieved with coplanar structure
[(b)] anticipated based on photocurrent density measured on new Cu(In,Ga)(S,Se)$_2$ materials
[(c)] projected from technoeconomic analysis using known thin film PV manufacturing costs (CdTe by First Solar)
[(d)] using 4% STH efficiency, 15x concentration, 270 S/m^2 for PEC material replaced every 2 years
TPD - tonne per day

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 $CuInGaSe_2$-based PV cells. An STH efficiency of 4% was achieved by our team in 2012 using a 1.6 eV bandgap $CuGaSe_2$ photocathode connected in series with three a-Si PV drivers (side-by-side architecture). The use of such coplanar architecture was dictated by the bandgaps of $CuGaSe_2$ that 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

PV-grade wide bandgap Cu(In,Ga)(S,Se)$_2$ absorbers. During this first year of our project, we have focused on the development of a baseline materials system to understand the basic properties and potential pitfalls of wide bandgap copper-chalcopyrites. Gallium-poor $CuInGaS_2$ thin films were fabricated using our two-step synthesis approach, in which a metal alloy with specific Cu, In and Ga composition is annealed under controlled sulfur atmosphere. Solar absorbers were then integrated as solar cells using a CdS layer to form a p-n junction, as well as resistive ZnO and conductive indium tin oxide transparent layers for electrical contact. Figure 1 presents the quantum efficiency (QE) measured on a gallium-poor $CuInGaS_2$ cell. At 550 nm, the conversion efficiency reaches a maximum of 68%. Then the QE drops suddenly, revealing possible recombination phenomena in the absorber. Eventually, the QE drops to zero at about 850 nm, a typical value for a Ga-poor $CuInGaS_2$ (1.53 eV bandgap). The photocurrent generated with such structure was 15 mA/cm^2. Our team is focusing now on widening the optical bandgap of $CuInGaS_2$ by increasing the gallium concentration, with a targeted bandgap of 1.8–2.0 eV.

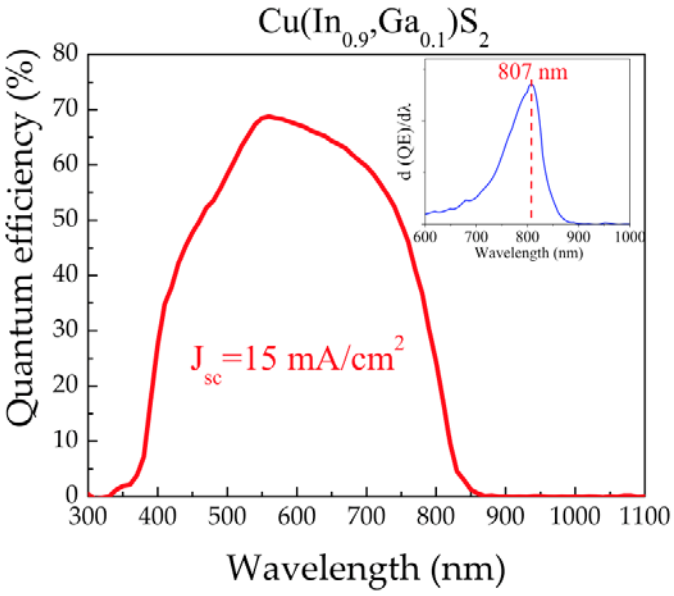

FIGURE 1. Quantum efficiency measured on $CuInGaS_2$-based solar cells

Subsurface energetics improvement: theoretical modeling. The development of a functional PEC device relies on the ability to efficiently separate and transfer photo-generated carriers to the catalytically active surface. Best performing $Cu(In,Ga)Se_2$-based devices typically employ CdS buffer layers due to a favorable conduction band offset. However, CdS does not form an ideal conduction band offset with wide bandgap sulfide alloys. This is illustrated in Figure 2, which shows the calculated band offsets of CdS relative to various chalcopyrites. While narrow bandgap $CuInSe_2$ and $CuInS_2$ have a moderate conduction band offset with CdS, a significant "cliff" is expected at the interface formed by intermediate bandgap $CuGaSe_2$ with CdS. A similar issue is likely to happen with wide bandgap $CuInGaS_2$ and CdS. Our results identify that the influence of Al incorporation, like Ga, is to primarily raise the conduction band of $CuInSe_2$ or $CuInS_2$. The degree that Al influences the conduction band position on an absolute energy scale and the resulting band offset with the buffer is expected to be more significant than for Ga, and offers alternative compositions

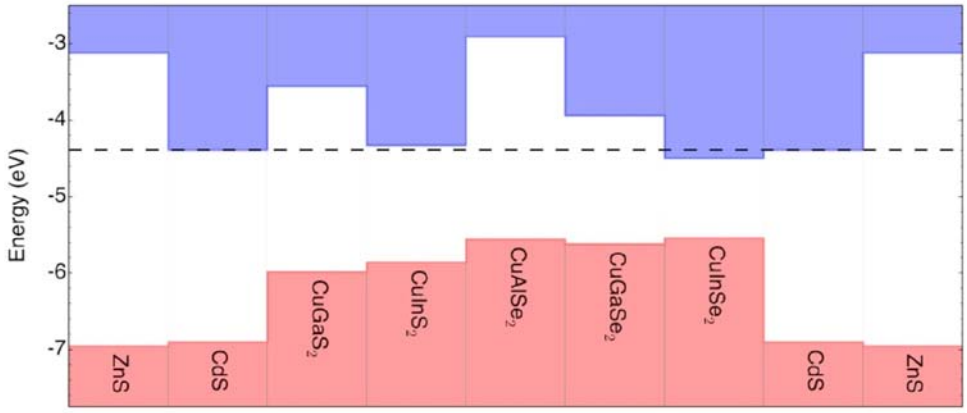

FIGURE 2. Calculated unstrained band offsets of CdS and ZnS with respect to various chalcopyrites

to $Cu(In,Ga)S_2$ alloys for targeting the desired 1.8–2.0 eV absorber bandgap of PEC materials.

Subsurface energetics improvement: advanced characterization. We utilized a suite of experimental techniques, both in the lab at UNLV and at Beamlines 8.0.1 and 9.3.1 at the Advanced Light Source (ALS), Lawrence Berkeley National Laboratory, to derive a comprehensive picture of surfaces and interfaces of the chalcopyrite-based PEC system. Experiments include in vacuo studies to investigate electronic structure properties and operando studies to gain insights into the chemical properties of electrolyte–solid interfaces. For example, we have used X-ray emission spectroscopy at the ALS to determine optimal film thickness for operando studies in our custom designed in situ cells. Furthermore, we have employed surface sensitive methods at UNLV to study a first sample set devoted to the optimization of sample handling procedures, film thicknesses, and detailed characterization parameters. As an example, Figure 3 shows the X-ray photoelectron spectroscopy survey spectra of a "bare" $Cu(In,Ga)S_2$ absorber and a "thick" CdS layer on top of a $Cu(In,Ga)S_2$ absorber. Next steps will include a detailed analysis and design of the next sample series for the in vacuo experiments at UNLV, as well as an experimental run at the ALS in September 2015, in which we will characterize the electrolyte–$Cu(In,Ga)S_2$ interface.

Surface catalysis and corrosion resistance. Cadmium sulfide (CdS) is a popular buffer layer material for forming a heterojunction in chalcopyrite materials but, like $CuGaSe_2$, is unstable in acid at the potentials of interest for hydrogen evolution. Protecting the CdS/$CuGaSe_2$ structure is important to achieve devices that can operate without degradation in an acidic electrolyte. Over the first year of the project, we have worked to engineer molybdenum disulfide (MoS_2) protective coatings to stabilize $CuGaSe_2$ absorbers in acid electrolyte. A 5-nm thick Mo metal layer was evaporated on the $CuGaSe_2$/CdS structure and then converted into MoS_2

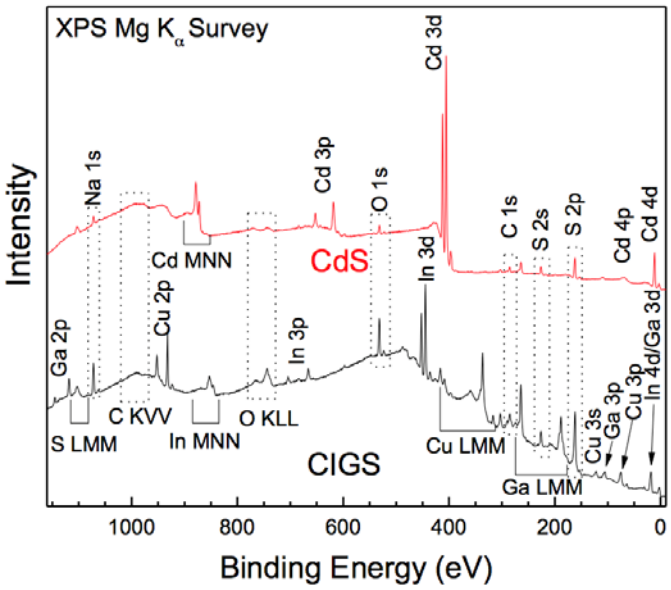

FIGURE 3. Mg Kα X-ray photoelectron spectroscopy (XPS) survey spectra of a "bare" $CuInGaS_2$ absorber and a CdS/CIGS interface sample

under H_2S atmosphere at 200°C. As shown in Figure 4, the electrodes with a MoS_2 protecting layer showed enhanced stability when compared with the unprotected CdS/$CuGaSe_2$ electrodes, though there is noticeable degradation from both the electrochemical measurements and X-ray photoelectron spectroscopy spectra. We hypothesized that the roughness of the $CuGaSe_2$ electrodes made complete protection by 5 nm evaporated films unfeasible and thicker films, which may protect the electrodes, would block too much of the incident light. We therefore turned to atomic layer deposition as a means to protect the electrodes. Initial tests demonstrated that atomic layer deposition is effective at coating WS_2 on rough $CuGaSe_2$.

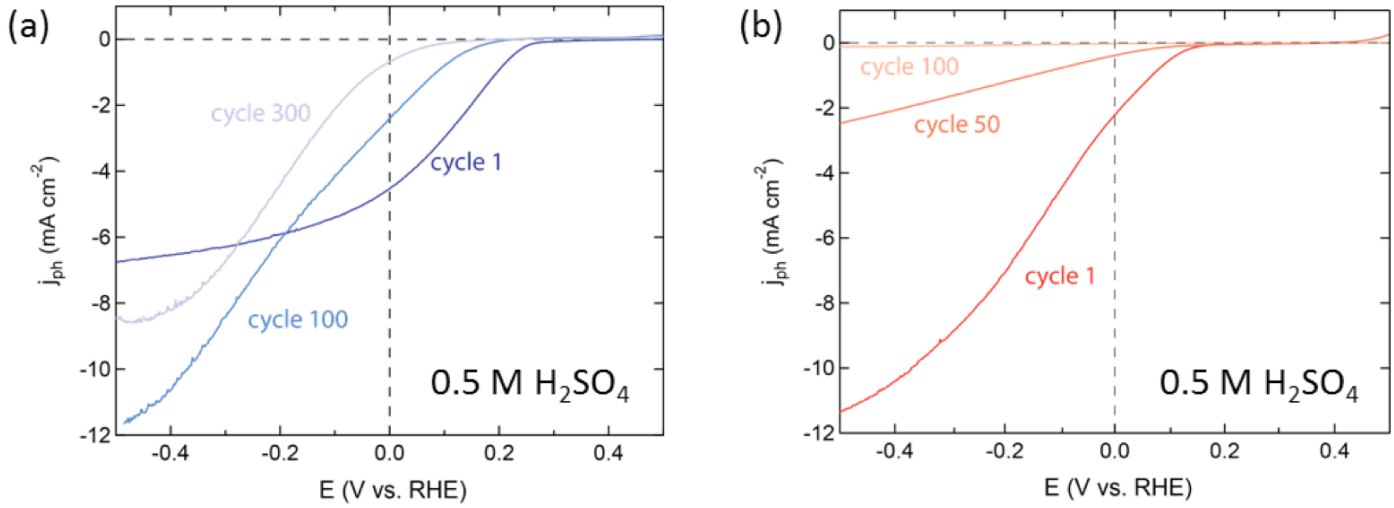

FIGURE 4. Photoelectrochemical activity and stability of (a) MoS_2/CdS/$CuGaSe_2$ electrodes and (b) CdS/$CuGaSe_2$ photoelectrodes in 0.5 M H_2SO_4

CONCLUSIONS AND FUTURE DIRECTIONS

- Cu(In,Ga)S_2 and CuGa(S,Se)$_2$ with controllable optoelectronic properties were successfully fabricated. In FY 2016, we will optimize our deposition processes to increase absorber efficiency.
- Cu(In,Ga)S_2-based solar cells with high open circuit potential (700 mV) have been achieved. In FY 2016, we will evaluate postdeposition treatments to passivate surface defects and develop alternative buffer layers to CdS.
- $CuGaSe_2$/CdS photocathode durability was enhanced with MoS_2. In FY 2016, highly conformal atomic layer deposition process will be improved to achieve pinhole-free MoS_2 layers.

FY 2015 PUBLICATIONS/PRESENTATIONS

1. Heli Wang, "Semiconductor Materials for Efficient Photoelectrochemical Water Splitting: The PEC Working Group," 249th ACS National Meeting, Denver, CO, March 22–26, 2015.

2. C. Heske, "Using Soft X-rays to Look into (Buried) Interfaces of Energy Conversion Devices," Chemical and Materials Engineering, University of Nevada, Reno, March 7, 2015 (invited).

3. N. Gaillard, "Wide Bandgap Chalcopyrite Photoelectrodes for Direct Solar Water Splitting," DOE Annual Merit Review Meeting, Arlington, VA, June 11, 2015 (invited).

4. N. Gaillard, A. Deangelis, M. Chong, and A. Zeng, "Development of Wide Bandgap Copper Chalcopyrite Thin Film Materials for Photoelectrochemical Hydrogen Production," Symposium J, MRS 2015 Spring Meeting, San Francisco (2015).