PDP_06_Kaneshiro

PHOTOELECTREMICAL HYDROGEN PRODUCTION

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MVSystems, Inc.
May 19, 2009

DE-FC36-07GO17105

Overview

Timeline

- Project start date: 9/1/2007
- Project end date: 8/31/2009
- Percent complete: ~65%

Budget

- Total project funding*
  - DOE share: **$1,358,827**
  - Contractor share: **$339,707**
- Funding received in FY08
- Funding for FY09 (tbd)

** funds cover work reported in posters PDP04, PDP05, and PDP06*

Barriers

•Barriers for photoelectrochemical hydrogen production technologies:

–Y: Materials Efficiency
–Z: Materials Durability
–AB: Bulk Materials Synthesis
–AC: Device Configuration Designs

Partners

- Collaborations: National Renewable Energy Laboratory (NREL), University of Nevada at Las Vegas (UNLV), Helmholtz Centre Berlin
- Project lead: MVSystems, Inc.

Overview

poster #PDP04
Progress in the Study of ***Amorphous Silicon Carbide*** as a Photoelectrode in Photoelectrochemical Cells

poster #PDP05
Progress in the Study of ***Tungsten Oxide Compounds*** as Photoelectrodes in Photoelectrochemical Cells

poster #PDP06
Progress in the Study of ***Copper Chalcopyrites*** as Photoelectrodes in Photoelectrochemical Cells

poster #PDP06

Progress in the Study of ***Copper Chalcopyrites*** as Photoelectrodes in Photoelectrochemical Cells

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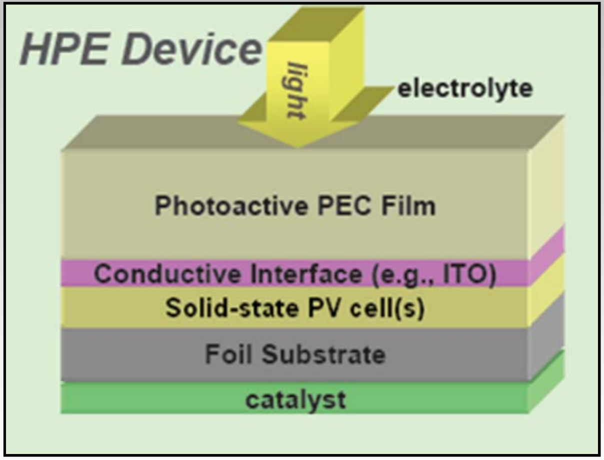
May 19, 2009

Relevance - Objectives

Develop copper chalcopyrite materials for incorporation into a hybrid photoelectrode (HPE) device capable of splitting water for hydrogen production when immersed in a suitable electrolyte and illuminated by sunlight.



Material Development

- Identify methods of increasing the bandgap of copper chalcopyrite films
  - To pass more light to an underlying PV cell
  - To possibly decrease valence band maximum, resulting in lower required voltage bias
- Make thinner copper chalcopyrite films
  - Pass more light to an underlying PV cell
- Surface modifications
  - Decrease required voltage bias
  - Improve surface kinetics
  - Increase durability

Device Development

- Use material development to synergize different components of HPE
  - Focus on decreasing required voltage bias
- Identify suitable underlying PV cells, possibly also copper chalcopyrite-based
  - Opto-electronically matched
  - Thermo-mechanically matched
- Identify suitable PEC-PV interfaces

Relevance

Milestones

Program targets	Copper Chalcopyrite progress status	
Year 1: 10/2007----9/2008		
✓ **Material Photocurrent ≥ 3 mA/cm²**	100% before project	Photocurrent is in excess with most copper chalcopyrite alloy compositions
✓ **Durability 100 hrs**	10% @ 6/2008	10hr durability achieved in 0.5M H_2SO_4 solution, no corrosion observed. *200hr. durability test pending with confidence
Year 2: 10/2008----10/2009		
✓ **Material Photocurrent ≥ 4 mA/cm²**	100% @ 10/2008	20 mA/cm^2 demonstrated with progressively thinner $CGSe_2$ films
✓ **Durability 200 hrs**	5% @ 1/2008	10hr durability still not contended, *200hr. durability test pending with confidence
✓ **Device STH efficiency ≥ 5%**	0% @ 3/2008	Device integration not achieved yet due to unsatisfied voltage requirements

(Towards the end of Year 2, a GO/NO-GO DECISION evaluation will be performed)

*Slide may change before AMR with updated durability figures

Approach

Using HFCIT Barriers as Guidelines

Barrier	Challenges	Strengths
Y. Materials Efficiency	– Misaligned band-edges (high VBM) – Correlations between material characterizations an device performance can be elusive	– Desirable optoelectronic properties – Synergy with copper chalcopyrite PV technology.
Z. Materials Durability	– Needs further exploration	– Operational stability for up to 4 hours – High degree of cycling stability
AB. Bulk Materials Synthesis	– High-temperature fabrication (T>500°C) – Uniform deposition of high quality films is difficult	– Some high-quality PV materials translate to high-quality PEC material. – Development of various fabrication methods
A.C. Device Config. Designs	– High-temperature fabrication (T>500°C) – Light transmission is insufficient for incorporation into a multijunction monolithic stack device – Misaligned band edges (high VBM) – High voltage bias required	– Thinner cells are still producing ample photocurrent – Great performance on TCO substrates – Sulfurization and surface modification studies are making progress in raising bandgap and optimizing band-edge alignment

Approach
Using Collaboration

THEORY

Effect of alloy compositions and surface treatments on material E_G and band-edges position.

CHARACTERIZATIONS

Photocurrent, Flat-band potential, OER/HOR, efficiency, morphology, advanced spectroscopy

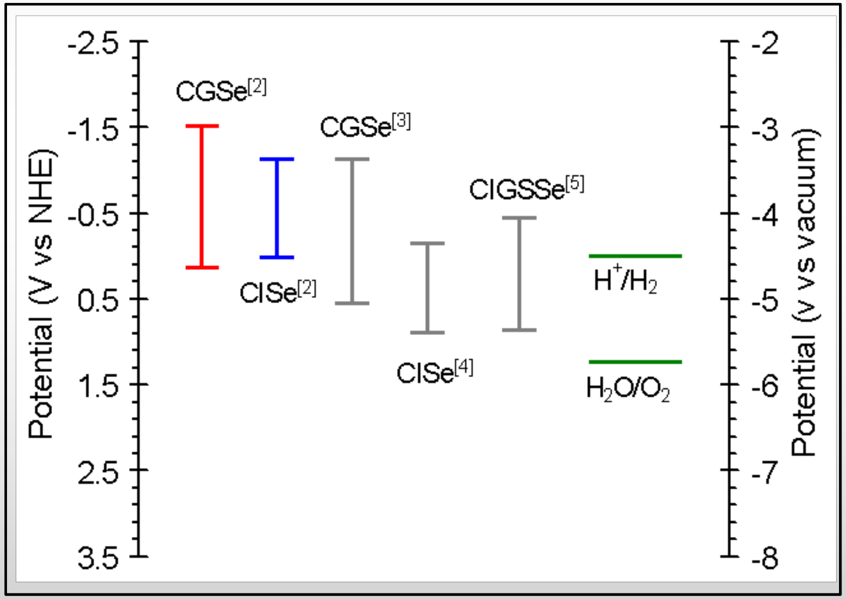
SYNTHESIS

Bulk materials, alloy compositions, sulfurization, surface treatment

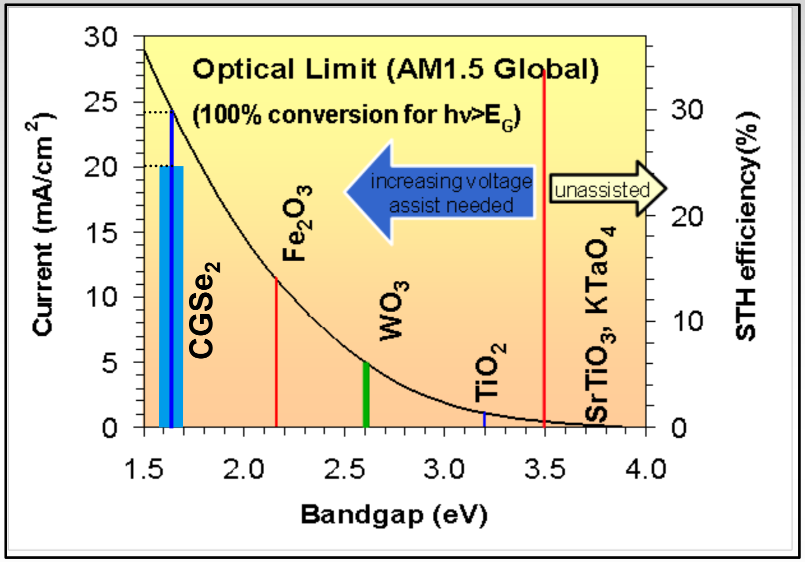
Focused Approach

Sacrifice excess current to improve band edge alignment

- Band edge misalignments increase required voltage bias
- Alloying stoichiometry and surface modifications may approve alignment.



1. E. L. Miller, IMRC XVI, October 2007
2. HNEI labs
3. Leisch & Turner, *ECS Abstract* (2006)
4. Siripala et. al., *Appl. Phys. Lett.* **62**, 519 (1993)
5. Weinhardt, Dissertation, U. Wurzburg (2005)



- Demonstrated photocurrents with $CGSe_2$ (thick light blue line over thin dark blue line) are in excess for our needs.
- Current can be sacrificed for improved band edge alignment and lower voltage bias requirements.

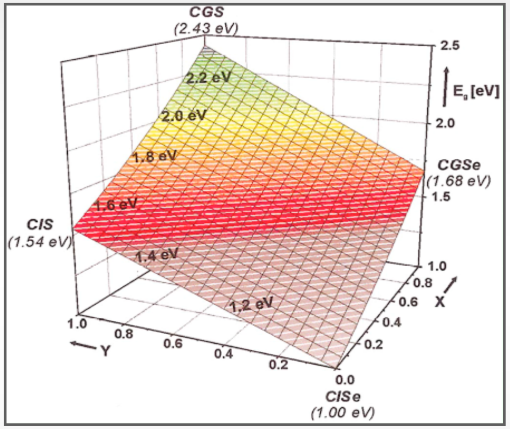
Progress

Analysis of Previously Reported Work

Previous investigations of this material for PEC water splitting experimented with effects of bandgap tuning as a function of alloy composition

- $CIGSe_2$
  - Produced very high photocurrents (barrier Y)
  - Corrosion and instability issues (barrier Z)
- $CI(S,Se)_2$ (contained sulfur and selenium)
  - Lower voltage onset (lower voltage bias required), indicating more favorable band-edge alignment (barrier AC)
  - Decreased photocurrent and bad fill factor (barrier Y)
  - Corrosion and instability issues (barrier Z)
- $CGSe_2$
  - Lower voltage onset (better band-edge alignment) than $CIGSe_2$ (but not $CI(S,Se)_2$, barrier AC)
  - Superior stability and durability (*very* low dark current, barrier Z)
  - Decreased photocurrent (barrier Y)

Bandgap Tuning in $Cu(In_{(1-x)}Ga_x)(S_ySe_{(1-y)})_2$



$CuInSe_2$ (E_G=1.0 eV)

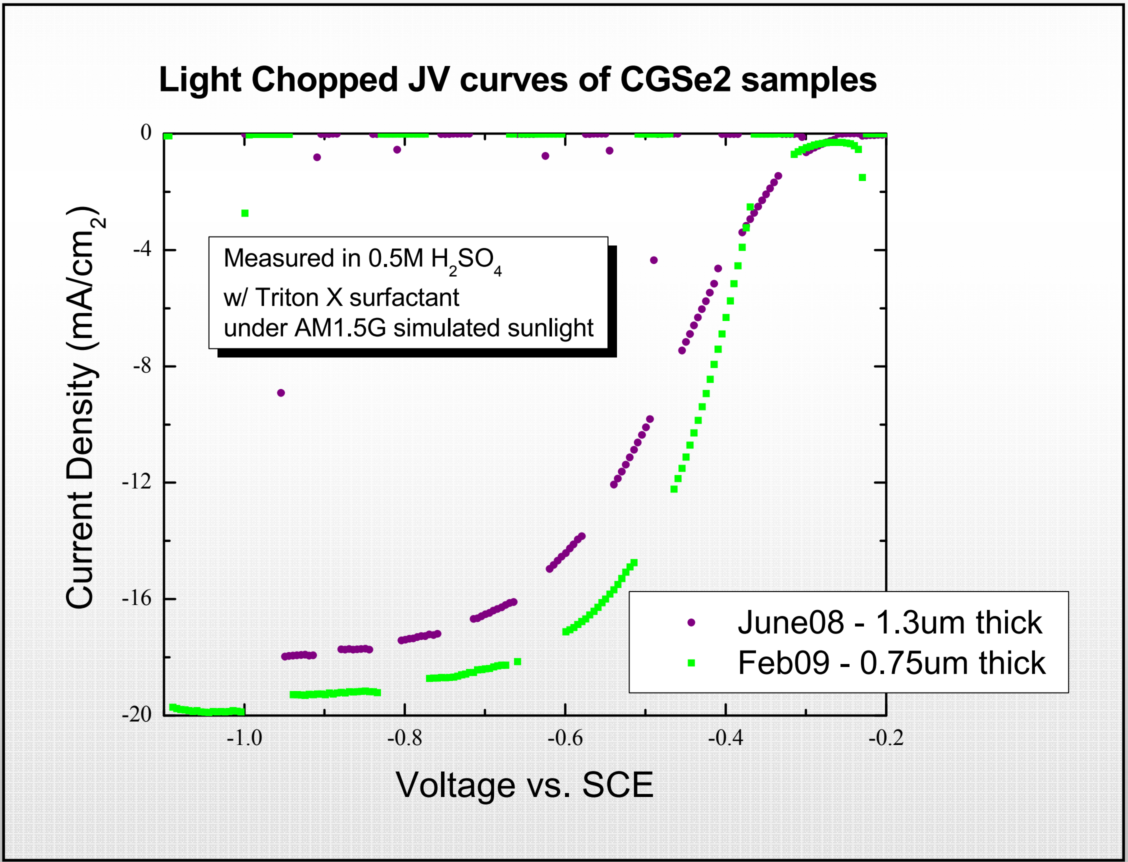
$CuIn_{0.4}Ga_{0.6}Se_2$ (E_G=1.4 eV)

$CuGaSe_2$ (E_G=1.68 eV)

$CuGaS_2$ (E_G=2.43 eV)

Progress
Improved Photocurrent (barrier Y)

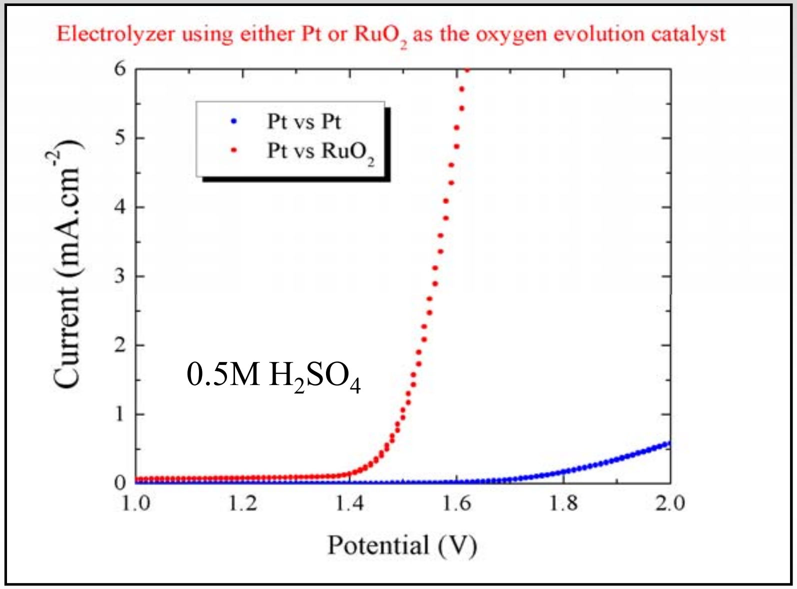
Fabrication process included a modified Se termination process at the end of the deposition, compensating for re-evaporation off heated substrate



- Standard $CuGaSe_2$ film performances improved nearly 11% with films that are almost 60% *thinner*
  - 18mA/cm^2, 1.3µm thick, June2008
  - 20mA/cm^2, 0.75µm thick, Feb2009
    - Improved “fill factor” as well
  - Decreased thickness means more available light transmitted for a PV bottom junction

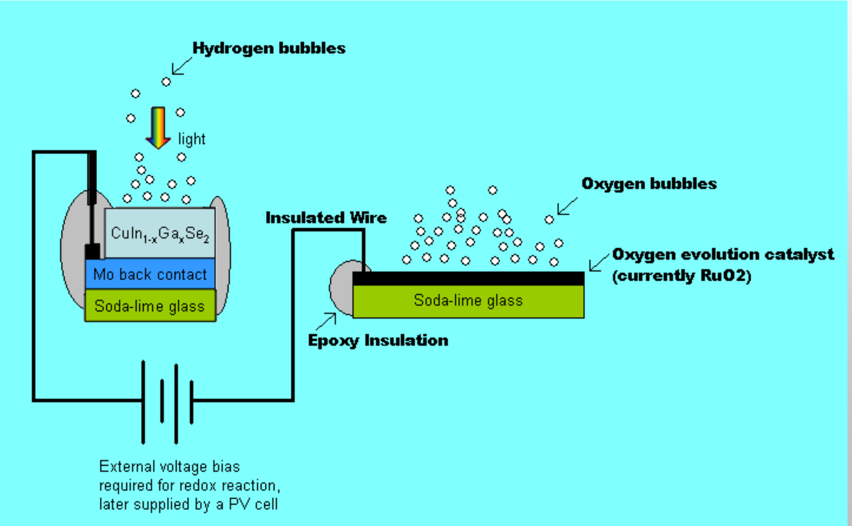
Progress

Counter Electrode (RuO_2 instead of Pt, barrier AC)



- Pt is not an ideal catalyst for O_2 evolution
- RuO_2 Preferred
  - Reactively sputtered films at HNEI outperform Pt as an O_2 evolution catalyst in an electrolyzer setup

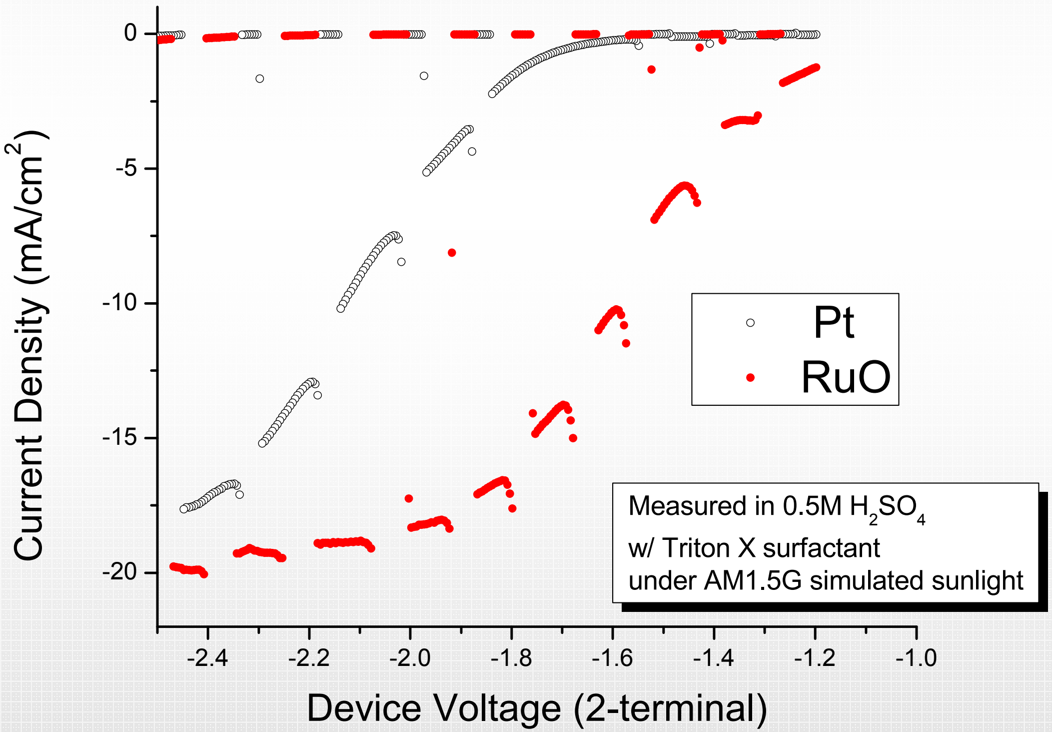
- Material testing configuration includes a reference electrode in electrolyte (3-terminal)
  - Does not include many of the effects of counter electrode
- Device testing (2-terminal) includes voltage drop across counter electrode
  - Elucidates effects of O_2 evolution



Progress

Counter Electrode (RuO_2 instead of Pt, barrier AC)

JV curves of one $CGSe_2$ sample run in a device configuration (2-terminal) using either a Pt or RuO_2 counter electrode



Experiments showed large voltage increase moving from 3- to 2-terminal operation.

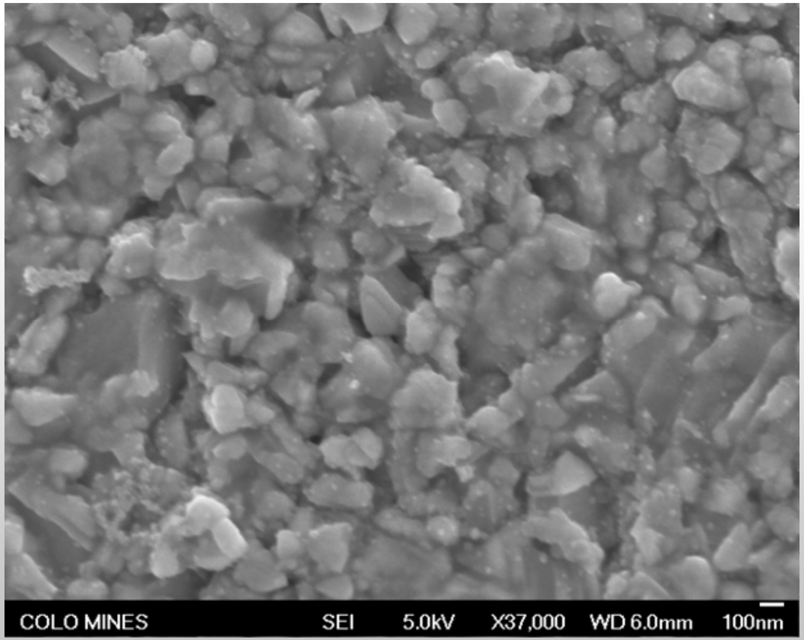
- Indicated large overpotential of O_2 evolution reaction (on counter electrode), not included in 3-terminal measurements
- Pt is a superior H_2 evolution catalyst
  - Not a very good O_2 catalyst
- RuO_2 shown in literature to be a better O_2 evolution catalyst
  - Reactively sputtered at HNEI
  - Experimentally verified (at left)

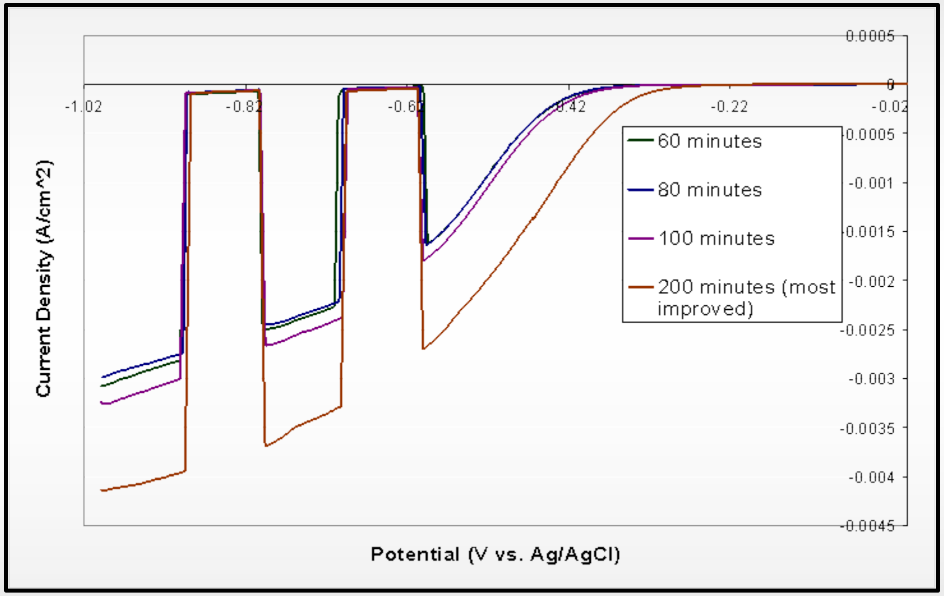
Progress

Platinization (collaboration with NREL, barriers Y, Z, AC)

NREL's Todd Deutsch, Kimberly See: Photoelectrochemical performance analysis of CGSe photocathodes platinized by electrodeposition and colloidal deposition

SEM images showing white dots not present before treatment that should be deposited platinum. EDS confirms presence of platinum.





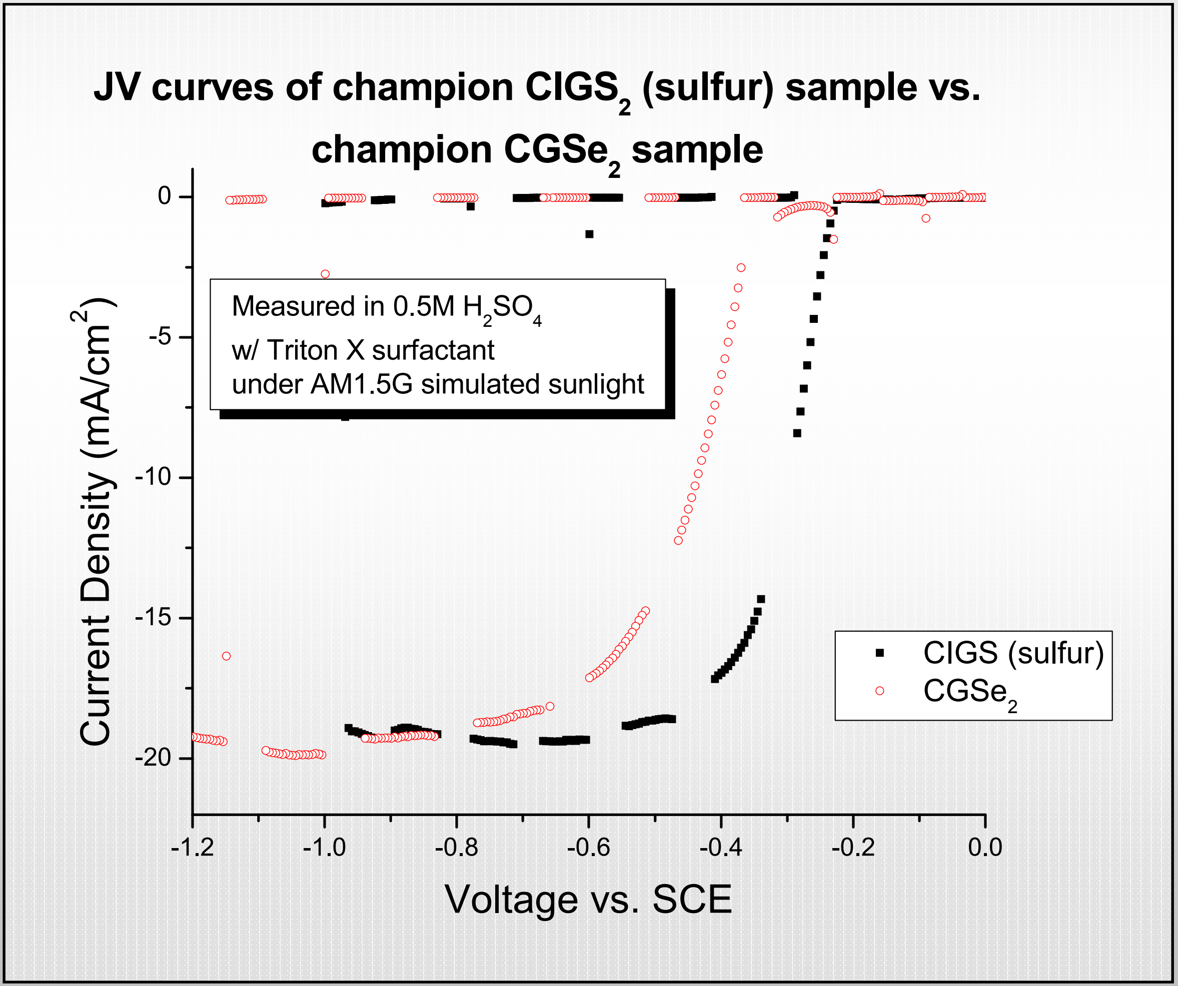
Improvements in LSV curves with soaking in commercially available colloidal platinum solution for different durations*

*Note: performance analyses were done using inferior $CGSe_2$ samples. New experiments are commencing using high-performance $CGSe_2$.

Progress

Sulfurization (Big Breakthrough! Barriers Y, AC)

Collaboration with Bjorn Marsen (formerly of HNEI), Helmholtz Centre Berlin



- *First shot* at $CIGS_2$ (sulfur completely replacing selenium) fabricated at the Helmholtz Centre Berlin decreases voltage onset vs. $CGSe_2$
- Indicates more favorable band-edge alignment (lower required voltage bias)

- Bandgap
  - $CIGS_2$ = 1.65eV
    - Determined by photocurrent spec. at NREL
  - $CGSe_2$ = 1.65eV
    - Determined by UV-Vis spec. at HNEI

Collaborations

- Partners:
  - US Department of Energy PEC working group: Leading task force on copper chalcopyrites
  - National Renewable Energy Laboratory (NREL): Material characterizations, PEC performance characterizations, surface modifications (platinization), material/device theory
  - University of Nevada at Las Vegas: Analysis of the surface energy band structure of new photoelectrode materials
  - Helmholtz Centre Berlin: New alloy composition (sulfurization) fabrication, material/device theory
  - MVSystems Incorporated: development of PV cell to demonstrate hydrogen production in a standalone configuration.
  - International Energy Agency/HIA/Annex 26: collaboration with international institutes and universities

Future Work

- **Utilize the array of characterization tools available**
  - *Establish band energy diagrams of the copper chalcopyrite material class*
  - *Determine the minimum achievable VBM*
  - *Include in-situ characterization of solid-liquid interface*

- **Continued exploration of sulfurization**
  - *Possibly decrease valence band maximum (VBM)*
  - *Reduce required voltage bias*

- **Optimization for device implementations**
  - *Find lower limit of thickness to find maximum light transmission while maintaining satisfactory photocurrent*
  - *Surface structures for favorable band-edge shifts and long-term stability*
  - *Film quality optimization to improve "fill factor"*
  - *Numerical modeling and analysis*

Copper Chalcopyrite Summary

- Relevance
  - Develop copper chalcopyrite thin films for use in photoelectrochemical (PEC) water splitting cells for hydrogen production
  - Out perform PV to hydrogen production through electrolysis
- Approach
  - Use existing knowledge of light harvesting with copper for chalcopyrites for PV applications to apply the material to a PEC system
  - Use specific guidelines of HFCIT barriers to focus research efforts
- Progress
  - Increased photocurrent, reduced voltage drop at counter electrode, and development of superior alloy compositions are bringing us closer to our goals
- Collaborations
  - Utilizing specific skills and capabilities offered by our collaborators at NREL, UNLV and the Helmholtz Centre Berlin, we can effectively pool our resources to effectively address key issues
- Future Work
  - Establish band diagrams and surface properties to understand every step of redox reaction and use new information to focus fabrication and device matching efforts effectively

Project Summary

➢Relevancy

The MVSystems/UH project is accelerating the development of **three important PEC thin-film materials classes** (a-SiC, WO3 and CGSe) with high potential for reaching DOE goals of practical PEC water-splitting.

➢Approach

Use existing knowledge of the three PEC thin-film materials and their PV performances to apply them to a PEC system for hydrogen production.

➢Progress

Items	Thin-film materials	2008			2009			Note
		Target	Achieved	Status	Target	Achieved	Status	
Material photocurrent	a-SiC	≥ 3 mA/cm^2	7-8 mA/cm^2	100%	≥ 4 mA/cm^2	7-8 mA/cm^2	100%	
	WO_3		2.8-3 mA/cm^2	100%		3.6 mA/cm^2	90%	
	CGSe		20 mA/cm^2	100%		20 mA/cm^2	100%	
Material/Device durability	a-SiC	≥ 100 hrs	100 hrs	100%	≥ 200 hrs	150 hrs	75%	
	WO_3		100 hrs	100%		100 hrs	50%	
	CGSe		10 hrs	10%		10 hrs	5%	
Device STH efficiency	a-Si/a-SiC				≥ 5%	1%	25%	H_2 production observed
	WO_3					3.2%	65%	expected from current matching
	CGSe							

Project Summary

➢ Collaboration

In order to promote the needed scientific breakthroughs in PEC R&D, collaborations have been developed within the US DOE PEC Working Group and with the IEA-HIA PEC Annex-26.

➢ Future work

(1)Further improve the properties of thin-film materials.
(2) Develop new surface modification techniques.
(3) Establish band diagrams for the thin-film photoelectrode/electrolyte system.
(4) New techniques will be used to evaluate PEC films interface @ UNLV and use new information to focus fabrication and device matching efforts effectively.
(5) Improve the PV performance of the thin-film solar cell used in the hybrid PEC device.