PD055

# PHOTOELECTROCHEMICAL HYDROGEN PRODUCTION

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MVSystems, Inc.
June 7, 2010

DE-FC36-07GO17105

# Overview

## Timeline

- Project start date: 9/1/2007
- Project end date: 12/31/2010
- Percent complete: ~75%

## Budget

- Total project funding*
  - DOE share: **$1,508,827**
  - Contractor share: **$415,128**

** funds cover work reported in posters PD053, PD054, and PD055*

## Barriers

- Challenges for photoelectrochemical hydrogen production technologies:

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

## Partners

- Collaborators:
  Hawaii Natural Energy Institute (HNEI)
  National Renewable Energy Laboratory (NREL)
  University of Nevada at Las Vegas (UNLV)
- Project Lead: MVSystems, Inc.

# Overview

poster #PD053
Progress in the Study of ***Amorphous Silicon Carbide***
as a Photoelectrode in Photoelectrochemical Cells

poster #PD054
Progress in the Study of ***Tungsten Oxide Compounds***
as Photoelectrodes in Photoelectrochemical Cells

poster #PD055
Progress in the Study of ***Copper Chalcopyrites*** as
Photoelectrodes in Photoelectrochemical Cells

poster #PD055

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

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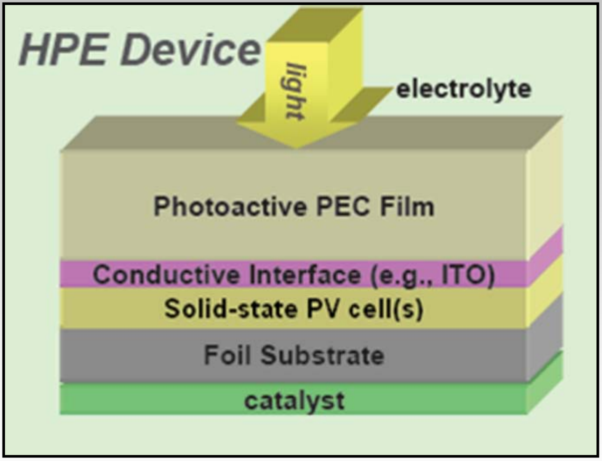
University of Hawaii at Manoa (UHM)

June 7, 2010

# 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 solar cell
- Surface modifications
  - Decrease required voltage bias
  - Improve surface kinetics
  - Increase durability
- Identify methods to move the valence band maximum lower
  - Ag in place of Cu
  - S in place of Se
  - Surface treatments

## Device Development

- Use material development to complement device development
  - Focus on decreasing required voltage bias
  - Explore possibility of serial coplanar devices
- Identify suitable underlying solar cells
  - Opto-electronically matched
  - Thermo-mechanically matched
- Identify suitable Solar cell/PEC Intermediate layer
  - Indium-Molybdenum Oxide, $MoSe_2$

# Relevance-Milestones

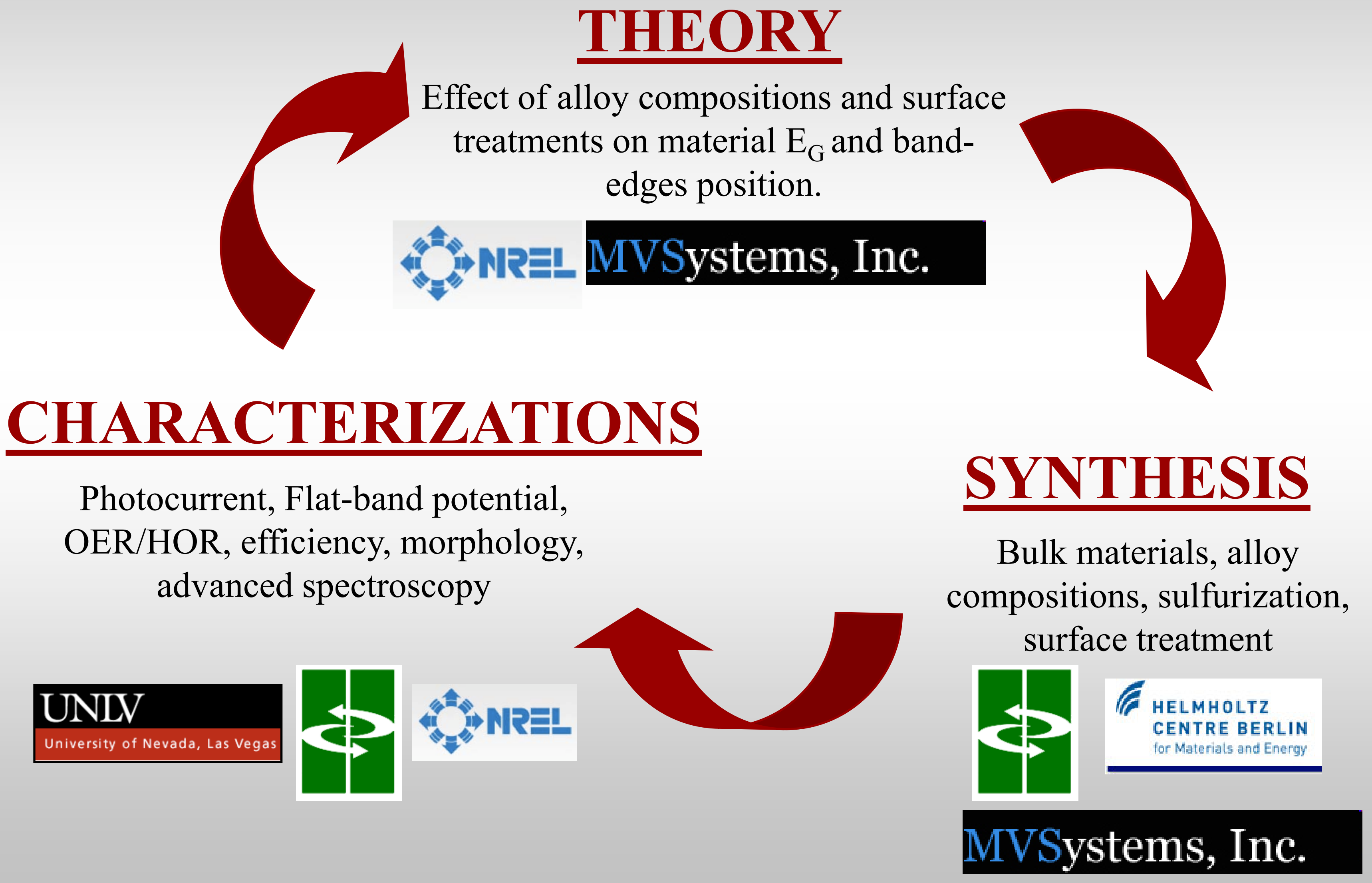
| Program targets | Chalcopyrite-based progress status | |
|---|---|---|
| **Year 1: (10/2007----9/2008)** | | |
| ✓ **Material photocurrent ≥ 3 mA/cm$^2$** | **100% @ 1/2008** | Photocurrents up to 13mA/cm$^2$ achieved |
| ✓ **Durability 100 hours** | **10% @ 6/2008** | 10 hr. durability test achieved |
| **Year 2: (10/2008----9/2009)** | | |
| ✓ **Material photocurrent ≥ 4 mA/cm$^2$** | **100% @ 1/2008** | Photocurrents up to 20mA/cm$^2$ achieved |
| ✓ **Durability: 200 hours** | **5% @ 6/2008** | Durability test not yet performed |
| ✓ **Device STH efficiency ≥ 5%** | **0%** | Material limitations precluded device |
| **Extended Year : (9/2009----12/2010)** | | |
| ✓ **Durability: 200 hours** | **5% @ 6/2008** | Test in progress at time of submission |
| ✓ **Device STH efficiency ≥ 5%** | ***0% @ 3/2010** | *Components available for multijunction device capable of ~5% STH efficiency (explained in slide 11) |

# Approach

## Using HFCIT Barriers as Guidelines

| Barrier | Challenges | Strengths |
|---|---|---|
| Y.<br>Materials Efficiency | – Misaligned band-edges (high VBM)<br>– Correlations between material characterizations and device performance can be elusive | – Desirable optoelectronic properties<br>– Synergy with copper chalcopyrite solar cell technology. |
| Z.<br>Materials Durability | – Needs further exploration | – Operational stability for up to 10 hours<br>– High degree of cycling stability |
| AB.<br>Bulk Materials Synthesis | – High-temperature fabrication (T>500 C)<br>– Uniform deposition of high quality films is difficult | – Silver incorporation could bring temperature down |
| A.C.<br>Device Config. Designs | – High-temperature fabrication (T>500 C)<br>– Misaligned band edges (high VBM)<br>– High voltage bias required<br>– Coplanar Serial Device divides current | – Great performance on TCO substrates<br>– Sulfur and/or Silver incorporation 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.

NREL
MVSystems, Inc.

## SYNTHESIS

Bulk materials, alloy compositions, sulfurization, surface treatment

HELMHOLTZ CENTRE BERLIN for Materials and Energy
MVSystems, Inc.

## CHARACTERIZATIONS

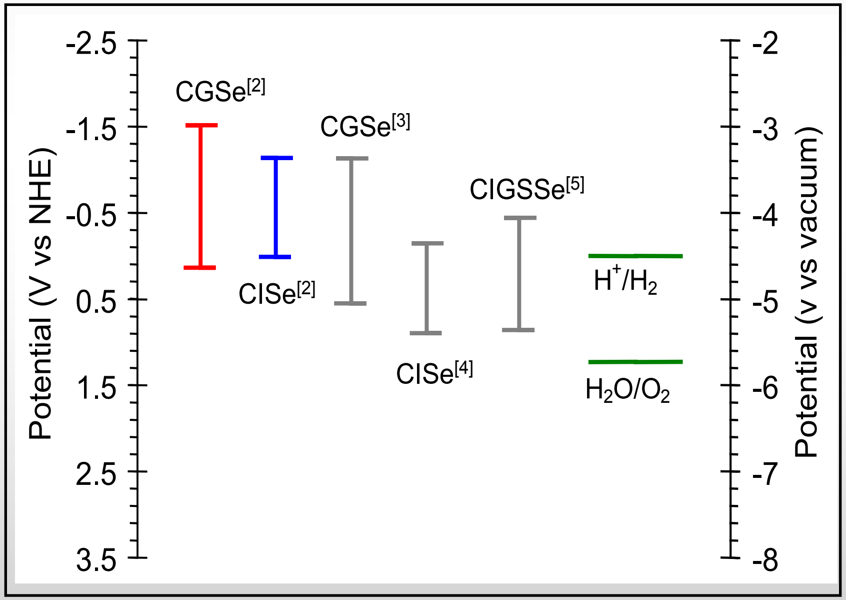
Photocurrent, Flat-band potential, OER/HOR, efficiency, morphology, advanced spectroscopy

UNLV University of Nevada, Las Vegas
NREL

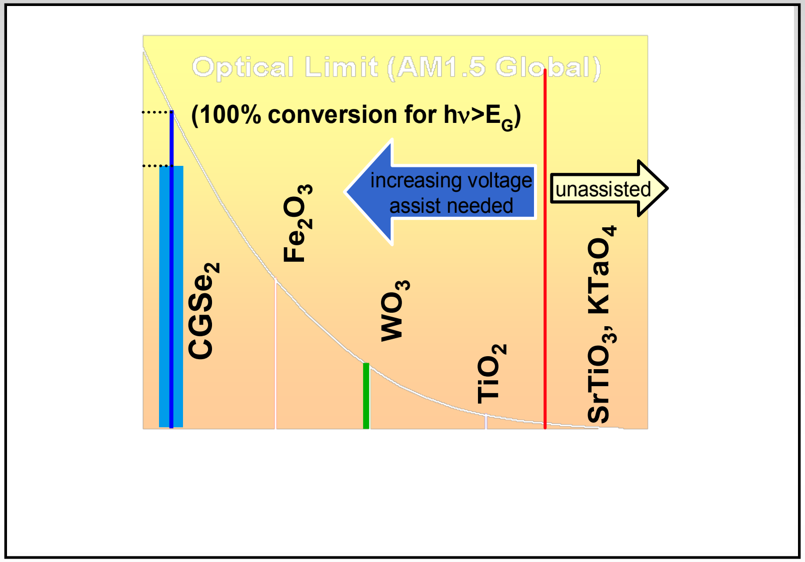
# Focused Approach

## Sacrifice excess current to improve band edge alignment

- Band edge misalignment increases 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 $CGSe_2$ and $CIGS_2$(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.

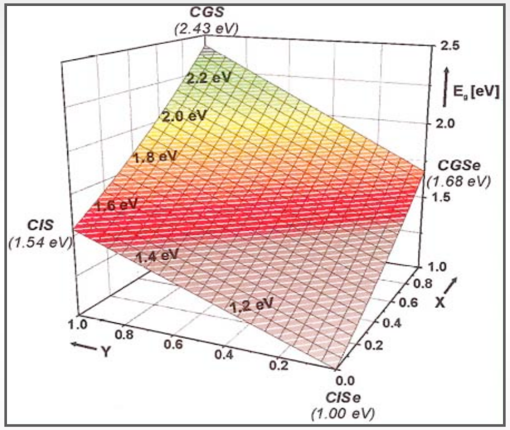
# Progress

## Status of existing materials

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

- $CIGSe_2$ (Process for Solar-grade films varied for PEC)
  - Produced very high photocurrents (barrier Y)
  - Corrosion and instability issues (barrier Z)
- $CGSe_2$ (Fabricated at HNEI)
  - Further lowered voltage onset for this material (improved fabrication procedure, barrier AC)
  - Superior stability and durability (*very* low dark current, barrier Z)
  - Voltage still too high (barrier AC)
- $CIGS_2$ (via Helmholtz Centre Berlin)
  - Lower voltage onset (lower voltage bias required), indicating more favorable band-edge alignment (barrier AC)
  - Photocurrent comparable to high-quality CGSe2 (barrier Y)
  - Not optimized for PEC (difficult to fabricate)

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



$CuInSe_2$ ($E_G$=1.0 eV)

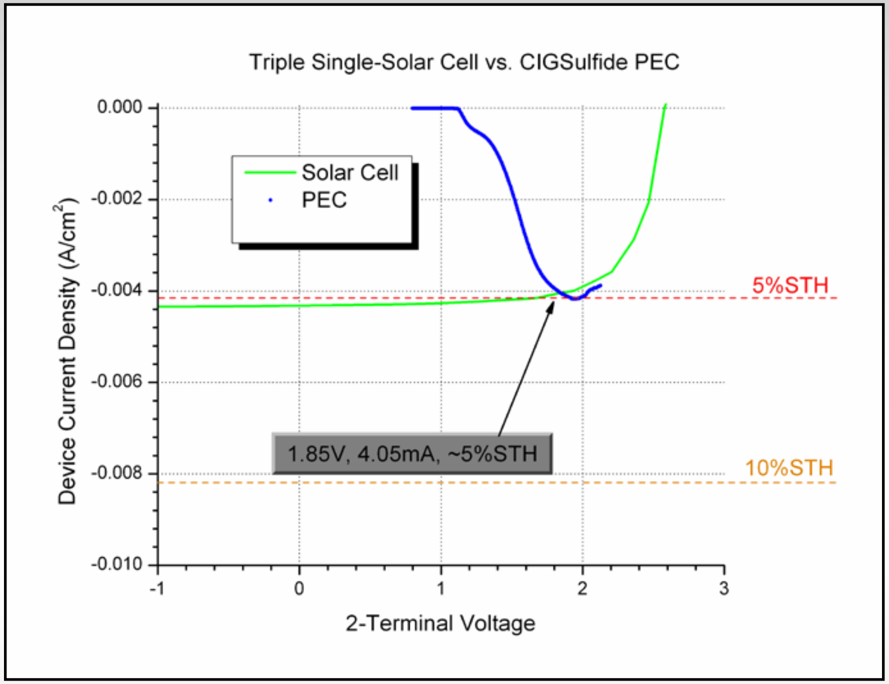
$CuIn_{0.4}Ga_{0.6}Se_2$ ($E_G$=1.4 eV)

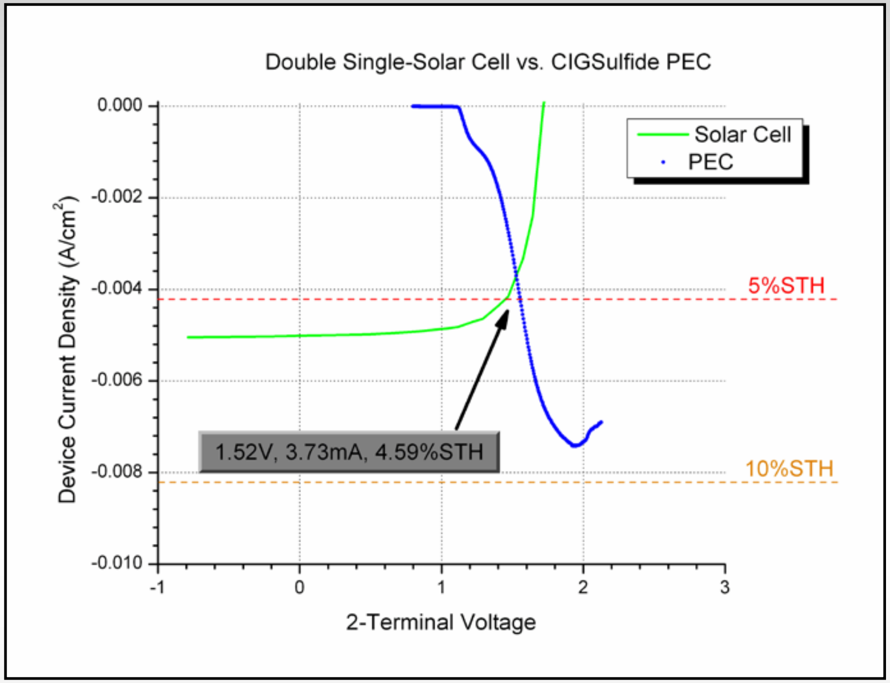
$CuGaSe_2$ ($E_G$=1.68 eV)

$CuGaS_2$ ($E_G$=2.43 eV)

# Progress

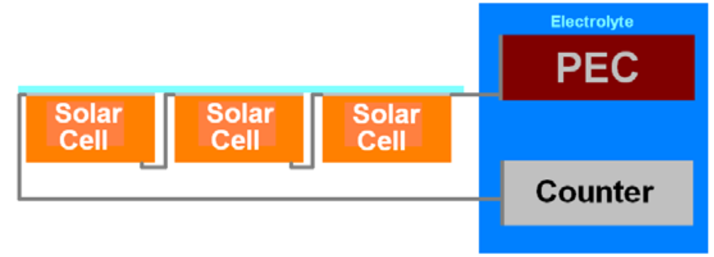
## Simulated* Co-Planar Hybrid Device





3x single-junction solar cell + PEC (4-junction) has slightly excess voltage. ~5% STH efficiency goal (~4mA/cm$^2$), but 4-junctions is not practical

2x single-junction solar cell + PEC (3-junction) could get higher STH efficiency if PEC onset voltage is improved



← Hybrid device: a-Si solar cells + PEC Device

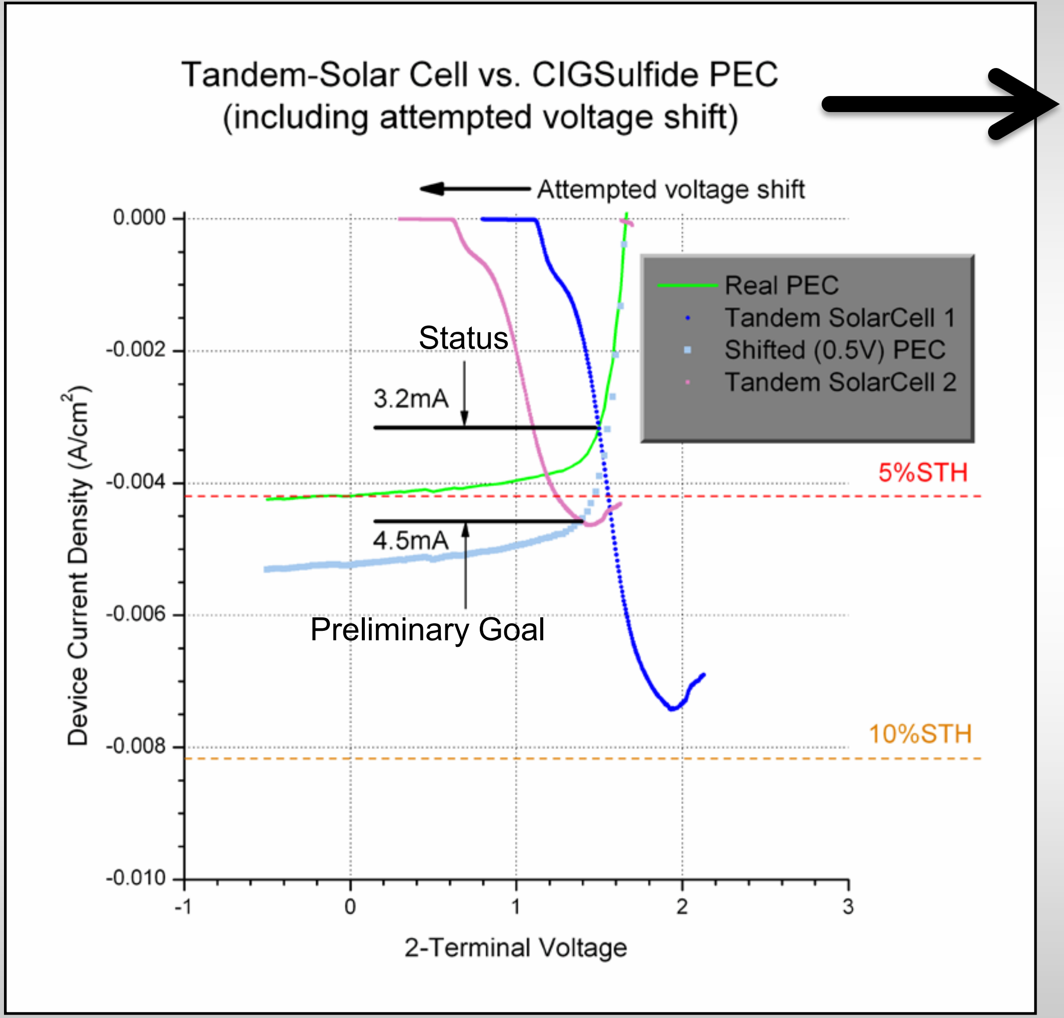
a-Si Solar Cells provided by MVSystems

CIGS$_2$ PEC cell provided by Helmholtz Centre

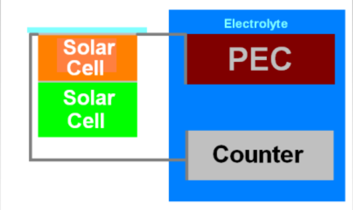
*Simulated by overlaying normalized operating curves of Solar and PEC devices

# Progress

## Co-Planar Hybrid Device to Monolithic Device



Blue PEC curve indicates as-produced PEC performance. The pink curve represents an attempted 0.5V shift (towards zero) which, with appropriate area ratio (Solar:PEC) optimization, can surpass 5% STH.



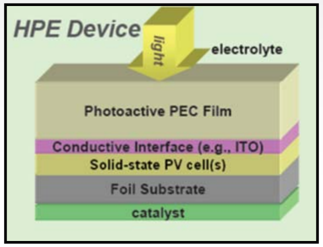
5%STH

Co-Planar Hybrid Device

as a pathway towards

a Monolithic Hybrid Photoelectrode

10%STH



### Preliminary Goal

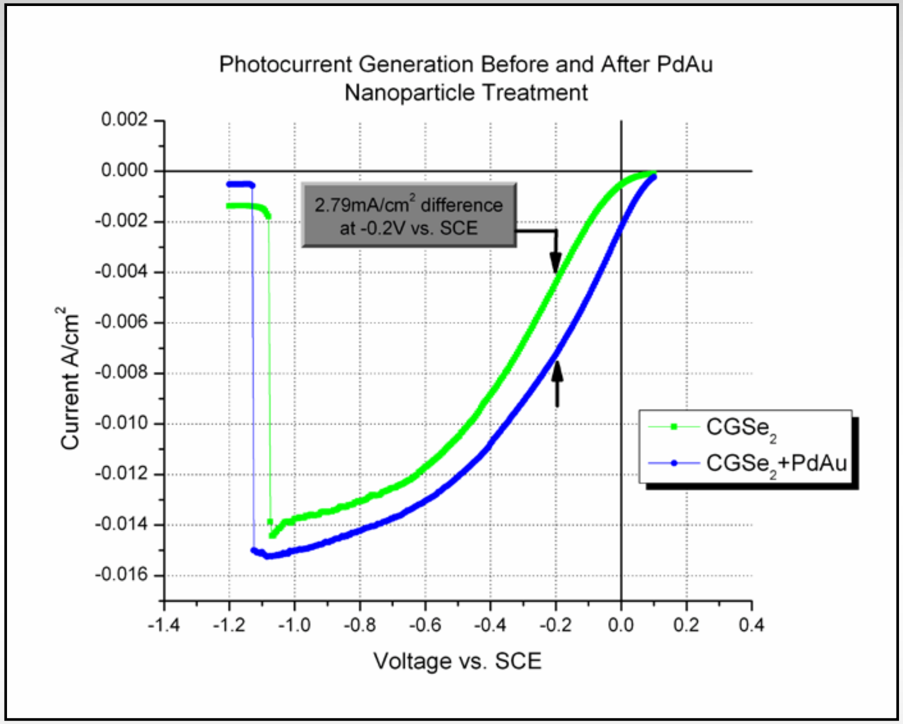
Achieve a voltage shift of ~0.5V (towards zero) to surpass 5%STH efficiency in a co-planar hybrid configuration with 3 junctions

### Real Goal

Use achievement to integrate PEC cell into a monolithic hybrid configuration to surpass 10%STH efficiency

# Progress

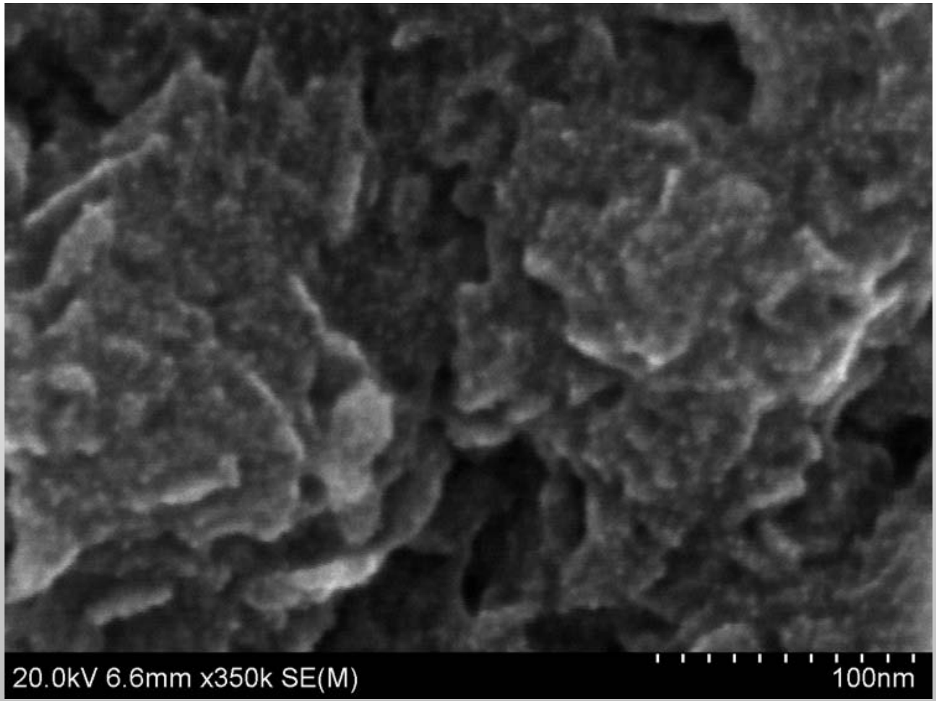
## Surface Treatments



### PdAu nanoparticles (sputtered)

Onset voltage and saturated photocurrent (not shown here) unchanged, but "fill factor" improved turn-on slope. Can be very valuable when integrated into a device.

- Presence of particles determined by SEM



Other Possible surface treatments

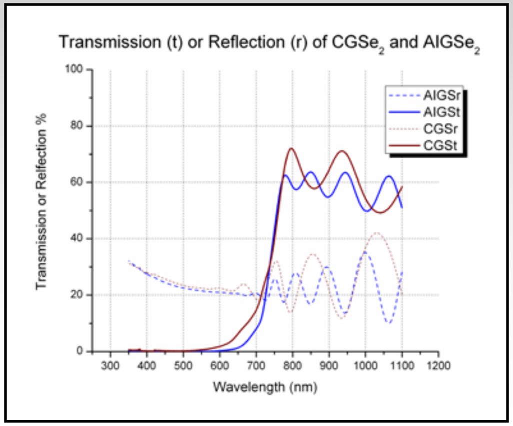
- CdS buffer layer (in progress, needs to operate in basic solution)
- Pt nanoparticles
- Partial surface etching

# Progress

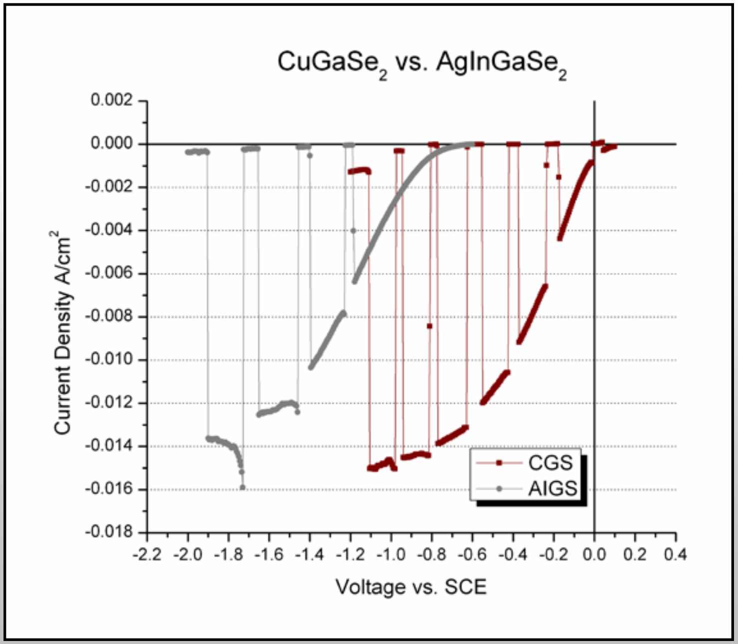
## Silver Incorporation (Partially or Fully Replacing Cu)

**Silver incorporation may lower the valence band maximum, hopefully providing a lower onset potential.**

- Also has higher bandgap
- Lower deposition temperature (useful in tandem fabrication)
- Expected drop in photocurrent (higher bandgap and diminished electronic properties)
- For full replacement of Cu with Ag, n-type conduction is expected (and verified by negative shift in open circuit potential upon illumination). Implications under investigation



UV-Visible photospectroscopy shows that the bandgaps are very similar



1st attempt to create AIGSe$_2$

- AgGaSe$_2$ segregates (AgSe$_2$ and GaSe$_2$)
- Ag drives bandgap up (presumably by lowering the valence band)
- In drives the bandgap down
- Comparable photocurrents, but onset voltage is worse
- Consider (Cu$_z$Ag$_{(1-z)}$) system

# Progress

## Back contact development as intermediate layer

$CGSe_2$ exhibits a large difference in voltage between 2- and 3-terminal measurements

- 3-terminal turn-on voltage of >0V vs. SCE reference electrode (in electrolyte at photocathode surface)
- 2-terminal turn-on voltage ~-1.2V (reference connected to counterelectrode)
- Use of $RuO_2$ instead of Pt for counterelectrode drastically improves turn-on voltage in 2-terminal measurement (but as expected, shows little change in a 3-electrode setup)
- $CGSe_2$ and related alloys typically exemplify extremely low dark currents indicating strong rectification; previously assumed to be good indication of corrosion resistance (shown in slide 14 JV curves) but may instead be due to impeded hole transport to back contact

Drawing analogies from Cu Chalcopyrites for Solar (especially tandem) applications

- Mo back contact shown to react with Se to form $MoSe_2$, aiding hole transport by acting as a quasi-ohmic contact
- Band alignment of Chalcopyrites with back contact TCOs (typically $SnO_2$:F in this project so far) may create a non-ideal junction requiring excess voltage to overcome
- Indium Molybdenum Oxide (IMO) being evaluated as candidate
- Thin Mo layer (5-10nm) on top of TCO before absorber layer deposition may selenize to form a sufficiently transparent $MoSe_2$ film

# 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 Solar cell to demonstrate hydrogen production in a standalone configuration.
  - International Energy Agency/HIA/Annex 26: collaboration with international institutes and universities

# Future Work

## Material

- 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*
  - *Perform 200hr. durability test (before AMR meeting)*
- Continued exploration of sulfurization and silverization
  - *Possibly decrease valence band maximum (VBM)*
  - *Reduce required voltage bias*
- Optimization for device implementations
  - *Surface structures for favorable band-edge shifts and long-term stability*
  - *More attention to back/intermediate contact*
  - *Film quality optimization to improve "fill factor"*
  - *Numerical modeling and analysis*
  - *Further develop device integration by reducing number of junctions required*

# Copper Chalcopyrite Summary

- Relevance
  - Develop copper chalcopyrite thin films for use in photoelectrochemical (PEC) water splitting cells for hydrogen production
  - Out perform Solar to hydrogen production through electrolysis
- Approach
  - Use existing knowledge of light harvesting with copper chalcopyrites for Solar applications to apply the material to a PEC system
  - Expanding use of electrochemical techniques to understand band diagrams and surface kinetics
  - Use existing approaches to tandem chalcopyrite Solar cells, as they also apply to our goal of a tandem hybrid Solar/PEC cell
  - Use specific guidelines of HFCIT barriers to focus research efforts
- Progress
  - Increased photocurrent, reduced voltage drop at counterelectrode, and development of superior alloy compositions and surface treatments has brought us to our goal of 5%STH efficiency in simulation.
  - Incorporation of Sulfur and Silver has lead to new materials that could potentially help us reach our goals
  - One surface treatment (PdAu nanoparticles) has already shown improved “fill factor”
- Collaborations
  - Utilizing specific skills and capabilities offered by our collaborators at MVSystems, 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 the 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, $WO_3$ and Chalcopyrite-based) with high potential for reaching DOE goals of practical PEC water-splitting.

- Approach

Use test protocols to measure optoelectronic properties of PEC material candidates using solid state integration to isolate the semicond./electrolyte interface (as introduced by MVS, PD053):

#1: Opto-electronic properties (Eg, dark and light conductivity, Fermi level position, extended state/hopping conduction) to match a set of predetermined criteria.
#2: Basic solid state Schottky barrier device for extraction of current
#3: Use semiconductor/electrolyte techniques at HNEI to match a set of predetermined criteria.

- 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.

# Project Summary

## ➢Progress

| Items | Thin-film materials | 2008 | | | 2009-2010 | | |
|---|---|---|---|---|---|---|---|
| | | **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%** |
| | $WO_3$ | | 2.9 mA/cm$^2$ | 90% | | 3.6 mA/cm$^2$ | 90% |
| | CGSe | | 20 mA/cm$^2$ | **100%** | | 20mA/cm$^2$ | **100%** |
| Material/Device durability | a-SiC | ≥ 100 hours | 150 hours | **100%** | ≥ 200 hours | 200 hours | **100%** |
| | $WO_3$ | | 100 hours | **100%** | | 100 hours* | 50% |
| | CGSe | | 10 hours* | 10% | | 10 hours* | 5% |
| Device STH efficiency | a-Si/a-SiC | ≥ 3.7% | 1% | 25% | ≥ 5% | 1.6%<br>*(6% projected from solid-state device perf.)* | 32% |
| | $WO_3$ | | 3.1% | 85% | | 3.1%<br>*(4.4% projected using 4-junction configuration)* | 62% |
| | CGSe | | 0% | 0% | | 0%<br>*(5% projected using 4-junction configuration)* | 0% |

* So far tested

## ➢ 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 Solar Cell performance of the thin-film solar cell used in the hybrid PEC device.

(6) Test of solid state device made of the PEC material of interest to evaluate its intrinsic optoelectronic performances.

**A Go/No Go decision will be made by the end of 2010.**