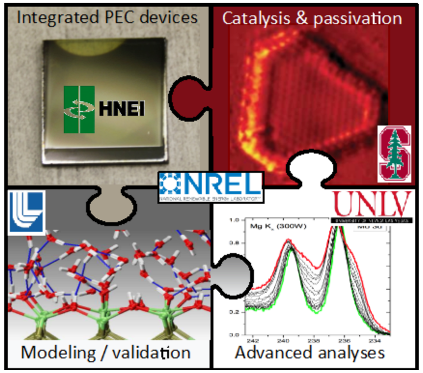
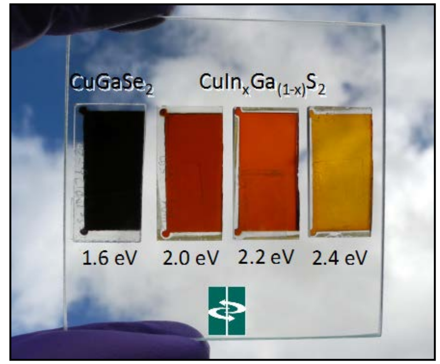
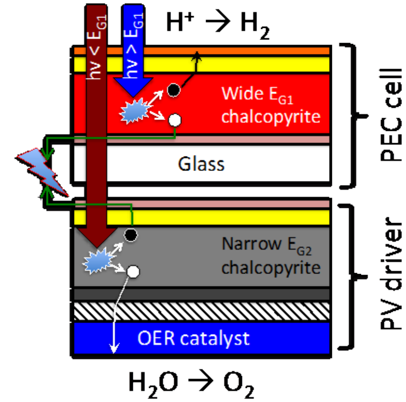






Wide Bandgap Chalcopyrite Photoelectrodes for Direct Solar Water Splitting

P.I.: Nicolas Gaillard
Hawaii Natural Energy Institute

2015 Doe Annual Merit Review
June 11th 2015

Project ID#: PD116

Overview

Timeline

- Project start date: 1/10/2014
- Project end date: 9/30/2017 *

* Project continuation and direction determined annually by DoE (Go/NoGo)

Budget

- Total budget funding: $3,000,000
  - DoE share: 100%
  - Contractor share: 0%
- Total DoE funds spent as of 03/2015 (including Nat. Labs): $250k

Barriers

Challenges for photoelectrochemical hydrogen production technology:

– Materials Efficiency (AE)
– Materials Durability (AF)
– Integrated device configuration (AG)
– Synthesis and Manufacturing (AJ)

Partners / primary role

- HNEI (N. Gaillard)
→ Absorber / p-n junction fabrication

- Stanford (T. Jaramillo)
→ Surface catalysis and corrosion protection

- UNLV (C. Heske)
→ Bulk/sub-surface/surface characterization

- LLNL (T. Ogitsu)
→ Absorber/interface theoretical modeling

- NREL (H. Wang, T. Deutsch)
→ Device validation and PEC reactor design

Relevance - Objectives

- **Long-term goal**: identify efficient and durable copper chalcopyrite-based materials which can operate under moderate solar concentration and capable of generating hydrogen via PEC water splitting at a cost of $2/kg or less.

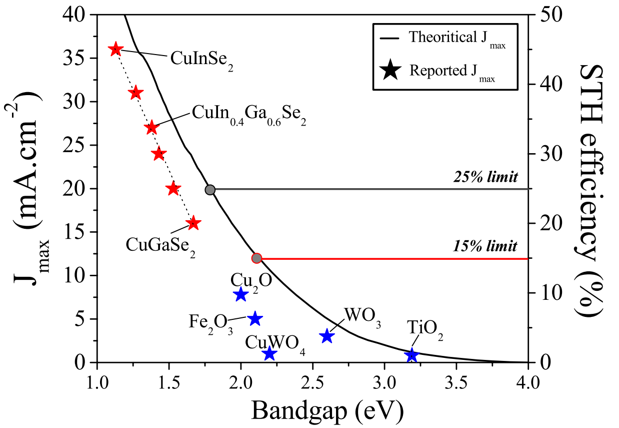
- **This project**: (1) develop new wide bandgap (>1.7 eV) copper chalcopyrites compatible with the hybrid photoelectrode (HPE) design, (2) demonstrate at least 15% STH efficiency and (3) generate 3L of H_2 under 10x concentration ("Type 4" PEC reactor) in 8 hours.

Table 3.1.8 Technical Targets: Photoelectrochemical Hydrogen Production: Photoelectrode System with Solar Concentration [a]

Characteristics	Units	2011 Status	2015 Target	2020 Target	Ultimate Target
Photoelectrochemical Hydrogen Cost [b]	$/kg	NA	17.30	5.70	2.10
Capital cost of Concentrator & PEC Receiver (non-installed, no electrode) [c]	$/m^2	NA	200	124	63
Annual Electrode Cost per TPD H_2 [d]	$/ yr-TPD$H_2$	NA	2.0M	255k	14k
Solar to Hydrogen (STH) Energy Conversion Ratio [e, f]	%	4 to 12%	15	20	25
1-Sun Hydrogen Production Rate [g]	kg/s per m^2	3.3E-7	1.2E-6	1.6E-6	2.0E-6

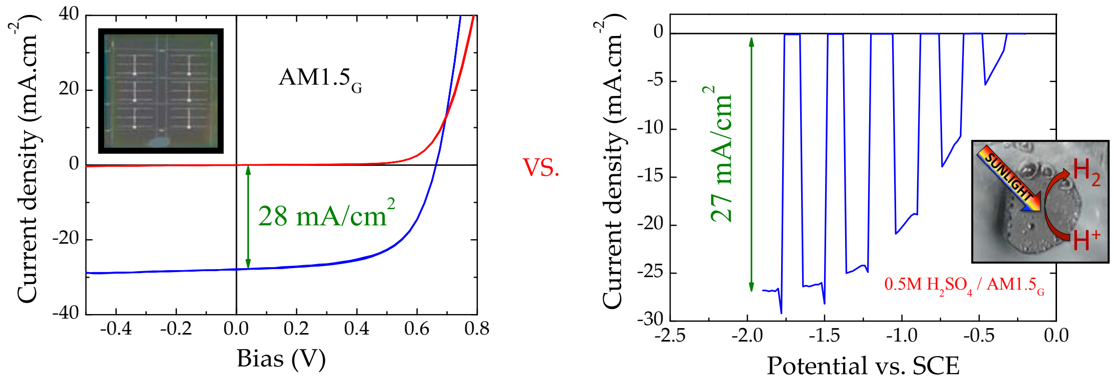
Relevance – Lessons learned from previous project

STH efficiency upper limit vs. absorber bandgap



Only PV-grade material classes can meet DoE targets

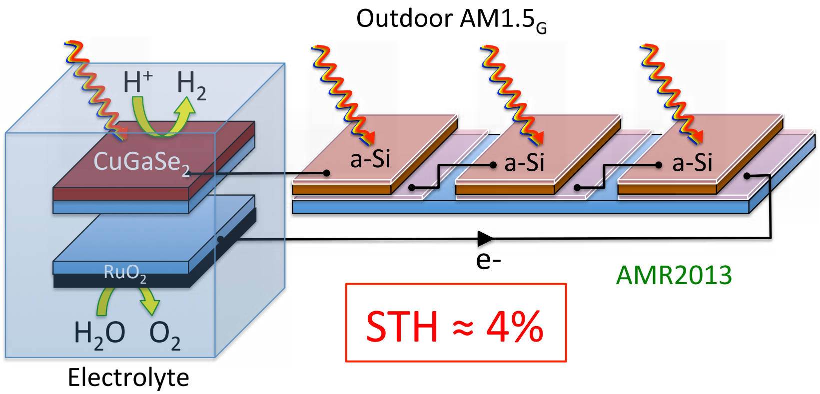
Photocurrent densities of 1.3 eV $CuInGaSe_2$ solar cell vs. PEC photocathode



Bandgap-tunable Cu-chalcopyrites make excellent candidates for PEC H_2 production

Standalone chalcopyrite-based PEC devices

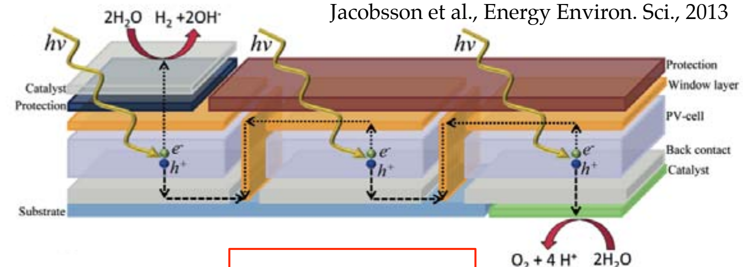
1.65eV $CuGaSe_2$-based standalone PEC device (HNEI/MVSystems)



STH ≈ 4%

AMR2013

1.1 eV $CuInGaSe_2$-based standalone PEC device (Angstrom Lab)



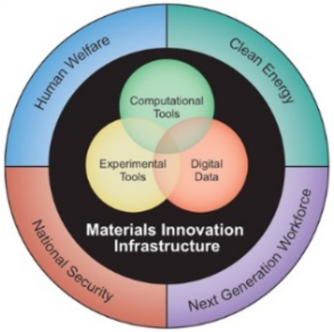
Jacobsson et al., Energy Environ. Sci., 2013

STH ≈ 10%

Take home message: Bandgaps of "conventional" copper chalcopyrites ($CuInGaSe_2$) are too narrow for efficient PEC H_2 production. New chalcopyrites with wider bandgaps are needed to relocate PV driver(s) under the photocathode (HPE structure).

Approach – Integrating experiment, computation and theory

Advanced Materials Manufacturing (AMM) / Materials Genome initiative (MGI)



Innovative materials discovery and development for faster product development. Key elements include:

- Integrating experiment, computation, and theory
- Making digital data accessible
- Creating a world-class materials workforce
- Leading a culture shift in materials research

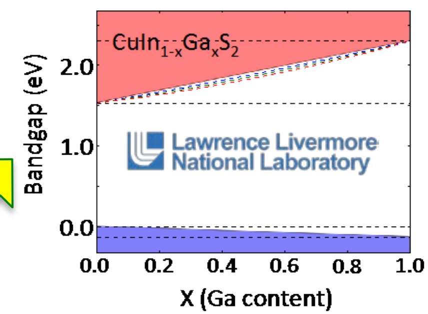
Accelerating materials development using integrated modeling, synthesis and advanced characterizations:

1. Bandgap calculation using reported values for known systems (data mining) or modeling of new semiconducting systems (to be uploaded to existing materials database),

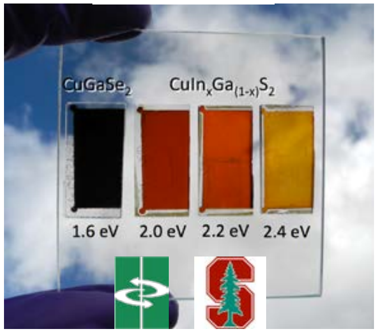
2. Theory-guided synthesis of wide bandgap chalcopyrites using state-of-the-art vacuum-based deposition tools,

3. Advanced surface and interface spectroscopy analyses of newly formed materials to validate modeling and refine synthesis.

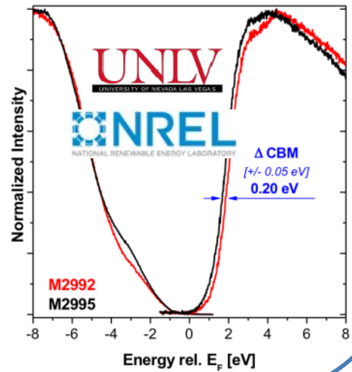
Modeling



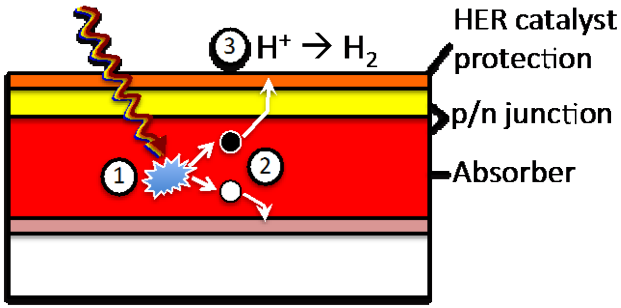
Synthesis



Characterization



Approach – Project tasks addressing barriers



PEC cell

Key steps in PEC H_2 production

① Photo-current generation (solid-state),
② Charge separation (solid-state),
③ Catalysis/durability (electrochemistry).

Task 1. PV-grade wide bandgap $Cu(In,Ga)S_2$ absorbers: **AE and AJ barriers**
Goal: identify, develop and test new wide bandgap material systems, supported by advanced characterization by theoretical modeling.

Task 2. Sub-surface energetics improvement (p/n junction): **AE and AG barriers**
Goal: identify, develop and test new “n-type buffers” compatible with wide Eg chalcopyrites, supported by advanced characterization by theoretical modeling.

Task 3. Surface catalysis and corrosion resistance: **AE and AF barriers**
Goal: evaluate Earth Abundant MoS_2 as both HER catalyst and protecting layer.

Task 4. Device certification and efficiency benchmarking: **AG barrier**
Goal: identify optical/electrical losses in complete HPE device made of HNEI’s CIGS and partners’ CIGSe, validate STH efficiency and quantify the volume of H_2 generated under 10x concentration in 8 hours.

Barriers list : AE: Materials Efficiency, AF: Materials Durability, AG: Integrated device configuration, AJ: Synthesis/Manufacturing.

Approach – Milestones

Task#	FY15 Milestones	Due Date	Status
1	Synthesize a $CuInGaS_2$ thin film material with controlled stoichiometry & microstructure	12/2014	100%
2	Fabricate $Cu(In,Ga)S_2$ cells with Voc> 600 mV	03/2015	100%
3	Durability > 500 hrs at 8 mA/cm^2 with a chalcorpyrite photoelectrode	06/2015	
4	Chalcopyrite photoelectrode with bandgap > 1.7eV that generates at least 10-12 mA/cm2	09/2015	
Go/No-Go decision criteria: Demonstrate a chalcopyrite photoelectrode material with bandgap > 1.7eV that generates a photocurrent density of at least 10-12 mA/cm^2			

Task#	FY16 Milestones	
1	$Cu(In,Ga)S_2$ solar cells with a photoconversion efficiency > 6%	12/2015
4	Photocurrent density relevant to 15-16% STH with chalcorpyrite 12-13 mA/cm^2	03/2016
3	Durability > 750 hrs at 8 mA/cm^2, with a stretch goal of 1,000 hrs	06/2016
2	Fabricate $Cu(In,Ga)S_2$ cells with Voc> 750 mV	09/2016
Go/No-Go decision criteria: Demonstrate a wide bandgap chalcopyrite-based heterojunction with an open circuit potential of at least 750 mV		

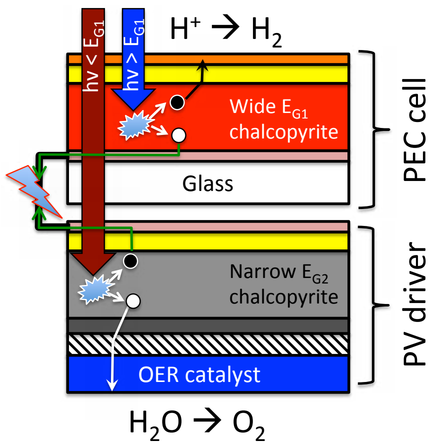
Task#	FY17 Milestones	
1	Photocurrent density relevant to 16-17% STH with a chalcopyrite 13-14 mA/cm2	12/2016
2	Fabricate $Cu(In,Ga)S_2$ cells with Voc> 900 mV	03/2017
3	Durability > 1,000 hrs at 8 mA/cm^2, with a stretch goal of 2,000 hrs	06/2017
4	HPE PEC device with a standalone STH of >15% generting at least 3L of H2 in 8 hrs.	09/2017

Accomplishments – Task 1: PV-grade absorbers

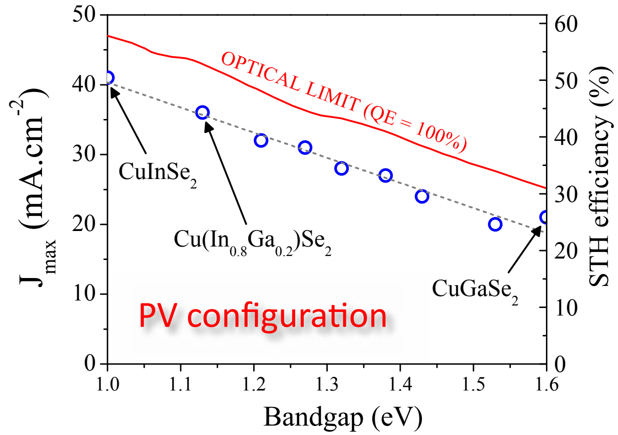
AE / AJ barriers

1. Identifying chalcopyrite material candidates with 1.8 eV <Eg < 2.0 eV

Proposed PEC device

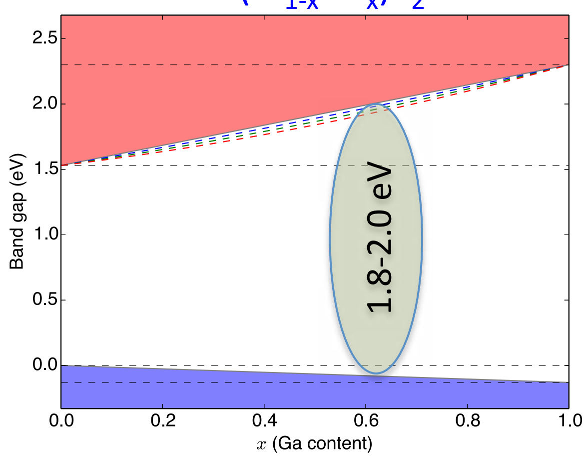


Adapted from Contreras et al., 37th IEEE PVSC (2011)



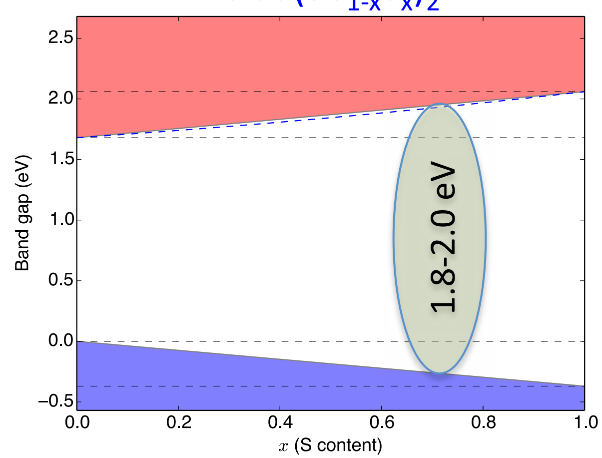
- PEC device: all-chalcopyrite dual absorber HPE,
- CIGSe ideal PV driver, but E_G too narrow for PEC,
- Absorber with $1.8eV<E_G<2.0eV$ required.

$Cu(In_{1-x}Ga_x)S_2$



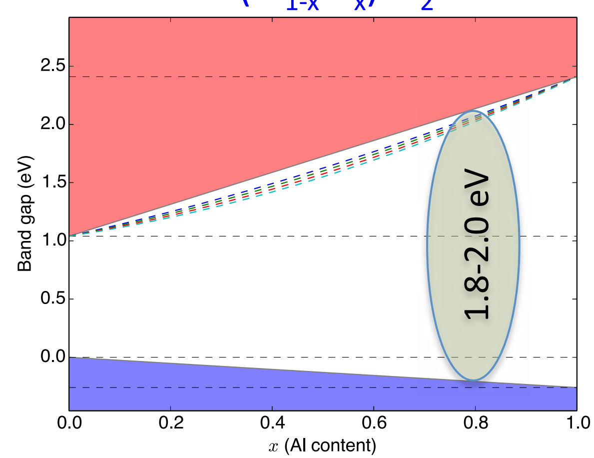
Proposed method: post dep. annealing

$CuGa(Se_{1-x}S_x)_2$



Proposed method: post dep. annealing

$Cu(In_{1-x}Al_x)Se_2$



Proposed method: direct co-evaporation

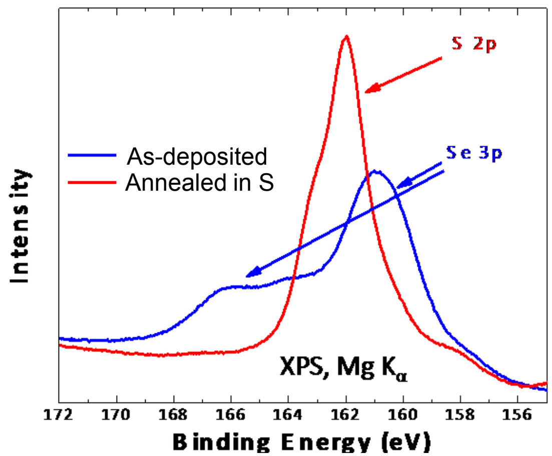
→ 3 alloys with great potential for PEC applications identified : $CuIn_{0.4}Ga_{0.6}S_2$ (today's presentation), $CuGaSe_{0.7}S_{0.3}$ & $CuIn_{0.2}Al_{0.8}Se_2$.

Accomplishments – Task 1: PV-grade absorbers

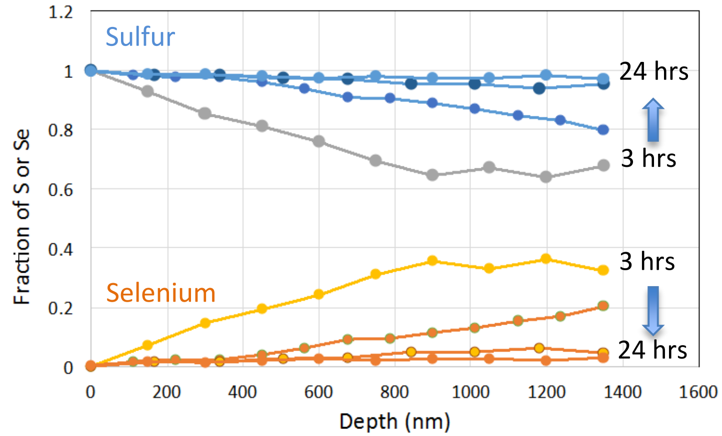
AE / AJ barriers

2. Proof of concept demonstration: sulfurization of $Cu(In,Ga)Se_2$

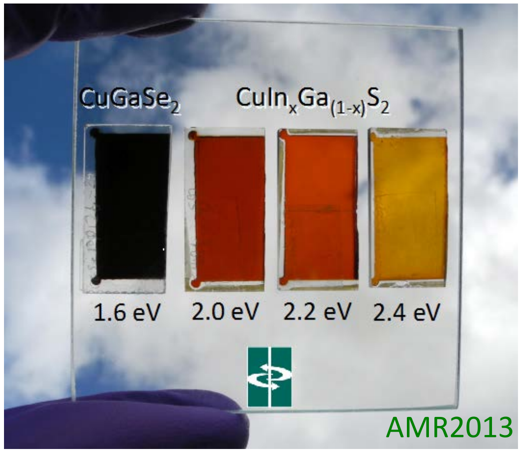
XPS on as dep. and sulfurized $CuInGaSe_2$



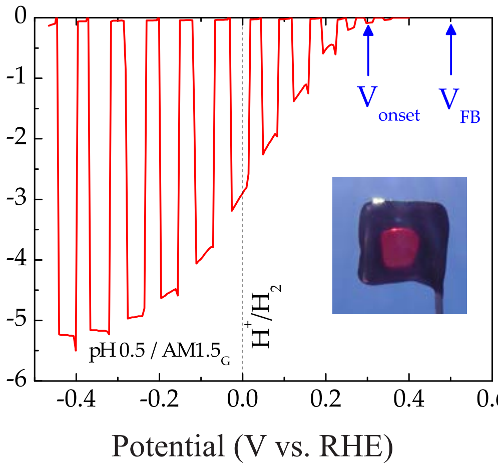
S and Se fraction vs. sulfurization time in H_2S



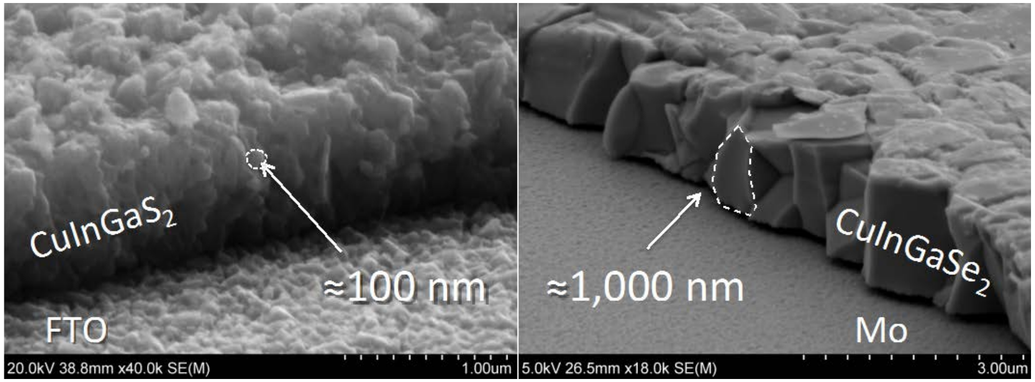
Pictures of wide Eg $Cu(In,Ga)S_2$



LSV measured on 700nm thick 2.0 eV $CuInGaS_2$



HNEI's PEC $CuInGaS_2$ vs. PV-grad $CuInGaSe_2$

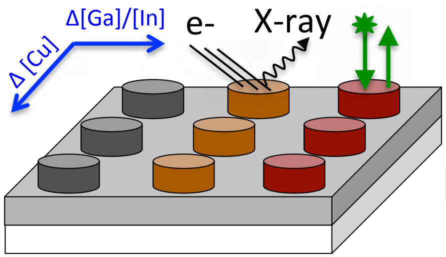


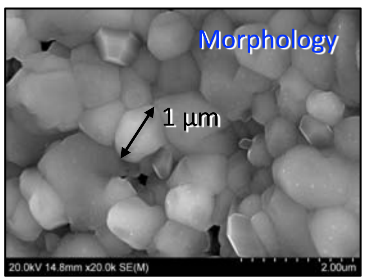
→ Successful fabrication of photoactive $CuInGaS_2$ with controlled composition and tunable bandgap (1.5 – 2.4eV).

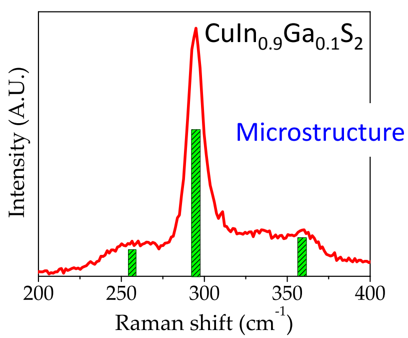
Accomplishments – Task 1: PV-grade absorbers

3. Accelerating PV-grade Cu(In,Ga)S_2 material development

Step1: Synthesis and characterization

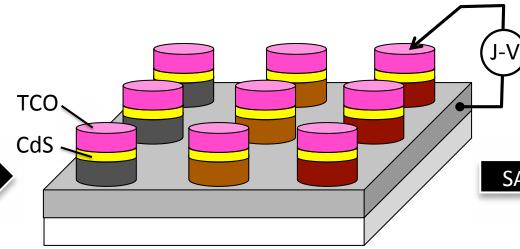


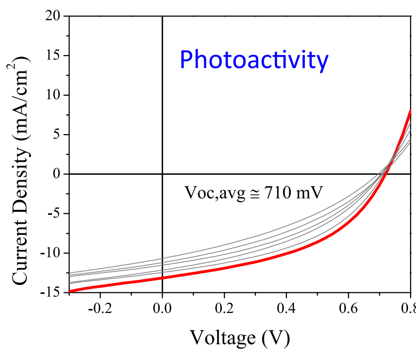


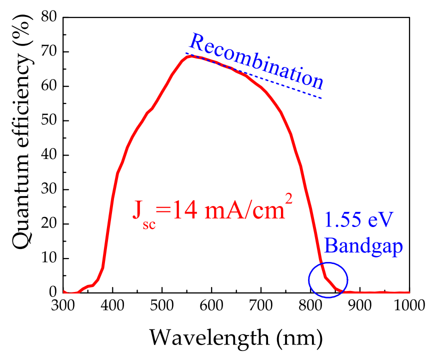


SAME SAMPLE

Step 2: Solid-state properties mapping

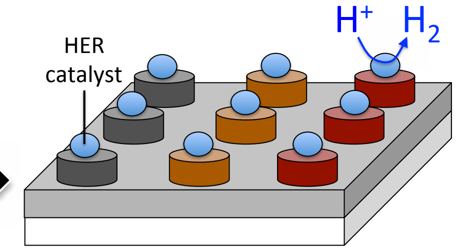


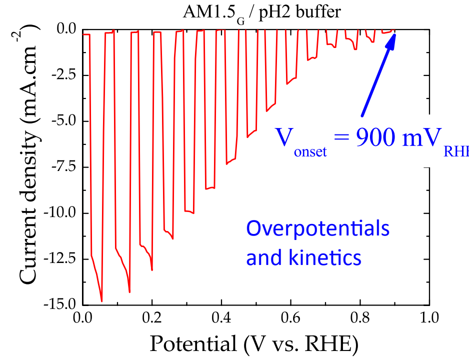


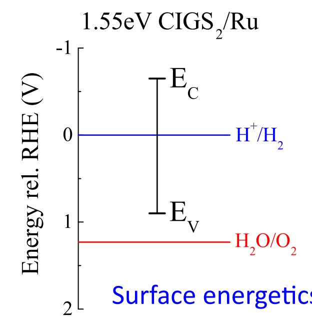


SAME SAMPLE

Step 3: PEC characterization







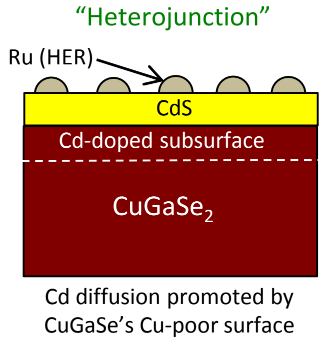
Take home messages:
- Three chalcopyrite (CIGS, CGSSe, CIASe) alloys identified with optimum bandgap energy for PEC applications,
- New synthesis/testing (solid-state & PEC) strategy developed to accelerate materials discovery,
- 1.55 eV PV-grade CIGS with great potential for PEC H_2 production successfully developed with this approach.

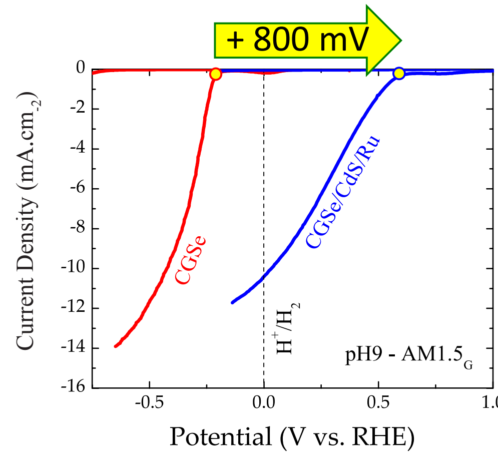
Accomplishments – Task 2: Sub-surface energetics

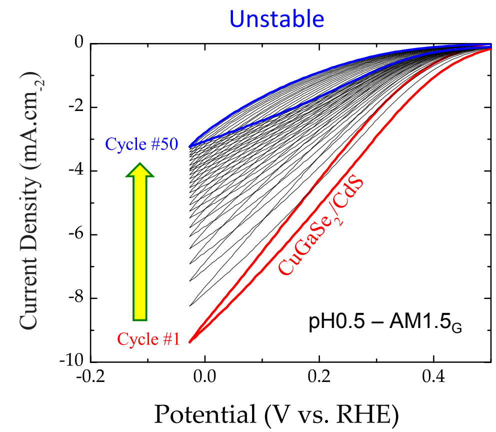
AE / AG barriers

1. Effect of n-type "buffers" on chalcopyrites PEC properties

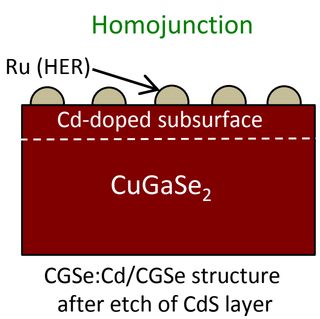
a. CdS (20 nm)/annealing (150°C in air)/Ru n.p. (PVD)

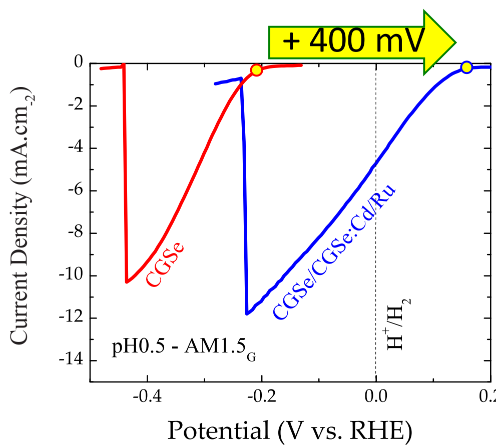


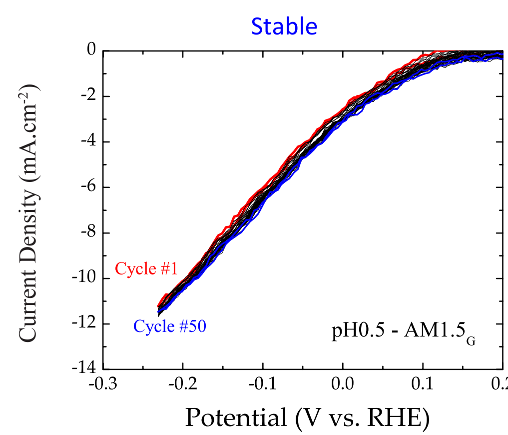




b. CdS (20 nm)/annealing (150°C in air)/**etch in HCl**/Ru n.p. (PVD)







→ Crucial role of both surface Cd doping (homojunction) and CdS layer (heterojunction) demonstrated for $CuGaSe_2$

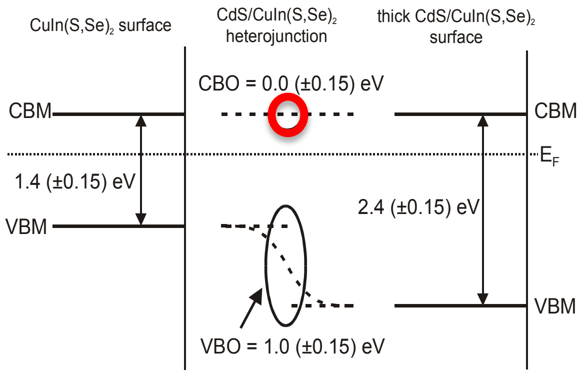
Accomplishments – Task 2: Sub-surface energetics

AE / AG barriers

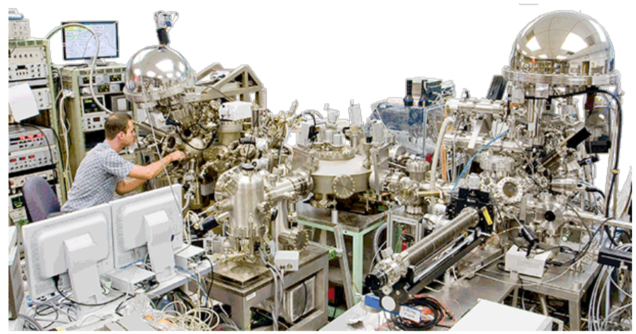
2. Identifying new buffers with optimum properties for wide E_G chalcopyrites (CBO = 0 eV)

a. Advanced surface and interface characterization

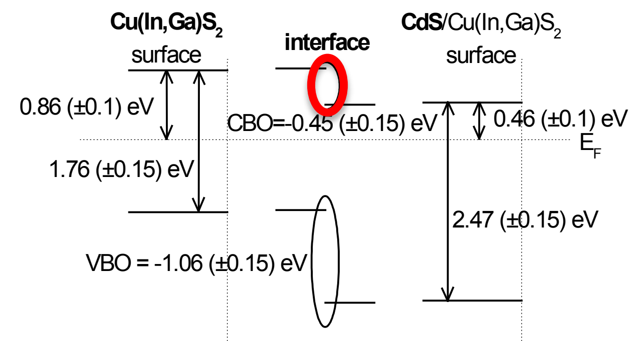
Narrow E_G $CuIn(S,Se)_2/CdS$
(previous study, not this program)



EuPVSEC17 (2001), p.1261



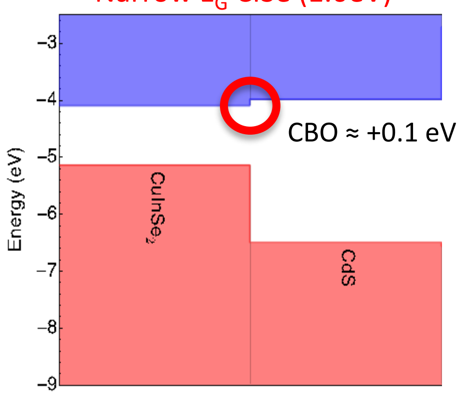
Wide E_G $Cu(In,Ga)S_2/CdS$
(previous study, not this program)



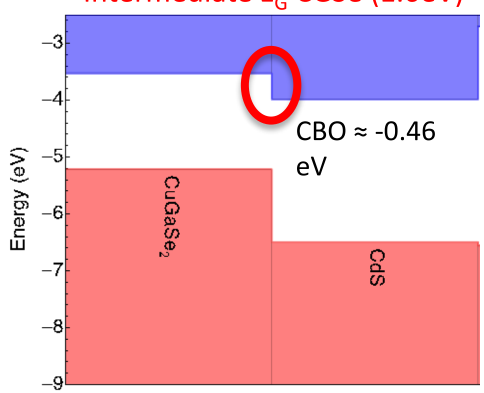
*APL **86**, 062108 (2005)*

b. Theoretical modeling

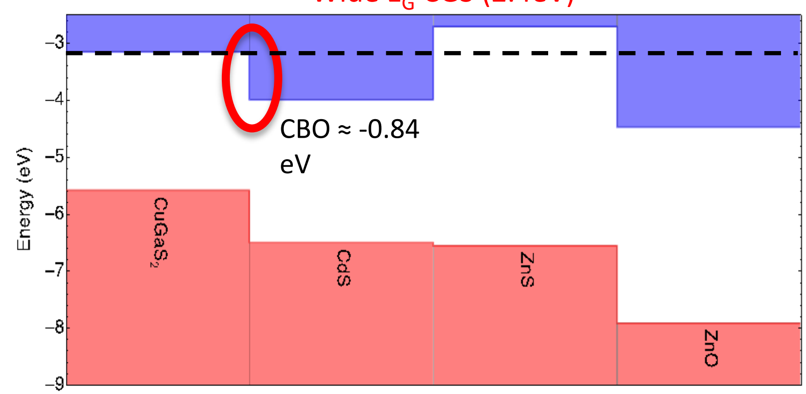
Narrow E_G CISe (1.0eV)



Intermediate E_G CGSe (1.6eV)



Wide E_G CGS (2.4eV)



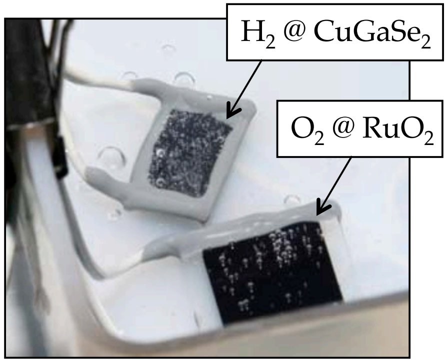
Take home messages:
- Cadmium sulfide surface energetics are not optimum for wide bandgap chalcopyrites,
- New buffers must be identified, synthesized, characterized and tested.

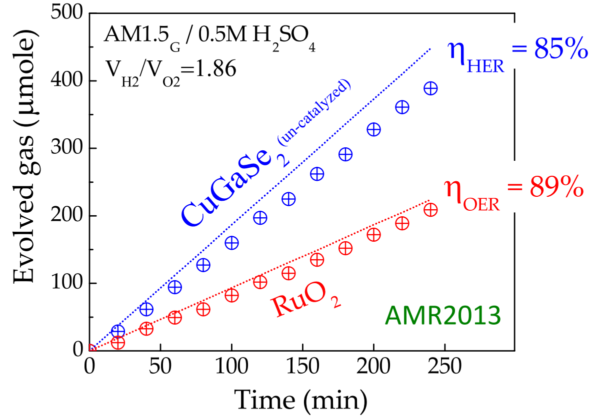
Accomplishments – Task 3: Surface catalysis/corrosion resistance

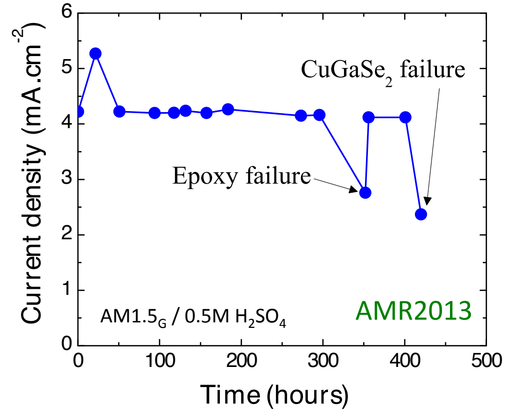
AE / AF barriers

1. Assessing the origin of chalcopyrite photocorrosion

a. Standard PEC tests in laboratory

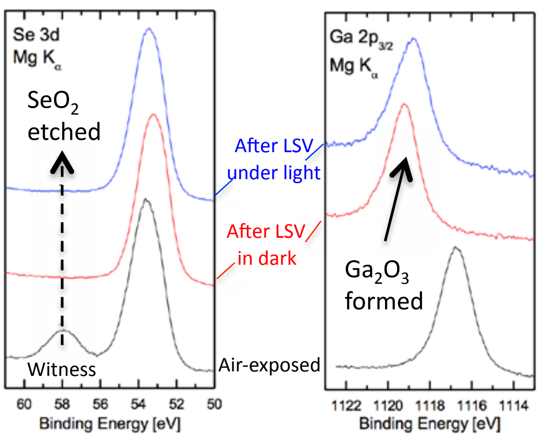






b. Advanced surface/interface characterization

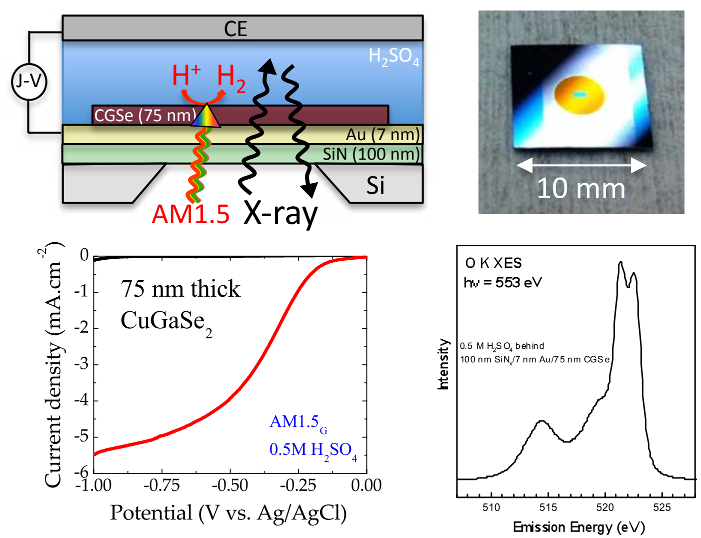
EX-SITU XPS (@UNLV)



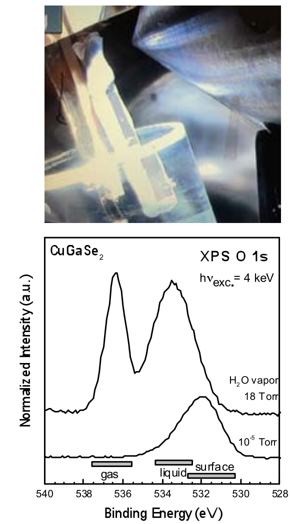
XPS analysis of $CuGaSe_2$ after PEC operation

Formation of unstable Ga_2O_3 at CGSe surface

IN-SITU XES (SALSA @ ALS, Berkeley)



IN-SITU Atm. Pressure XPS (ALS)



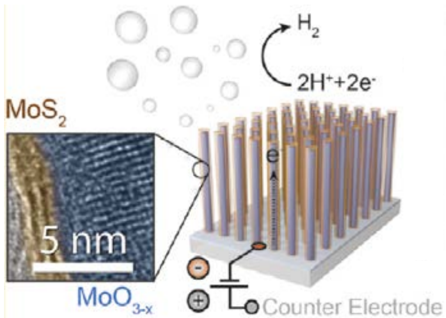
Element-specific bonding evolution under PEC operation

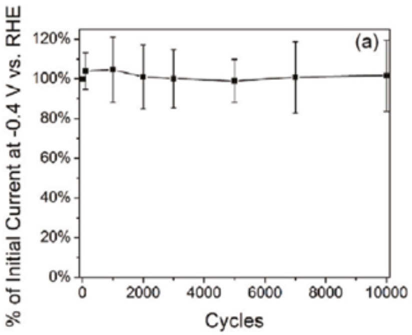
Accomplishments – Task 3: Surface catalysis/corrosion resistance

AE / AF barriers

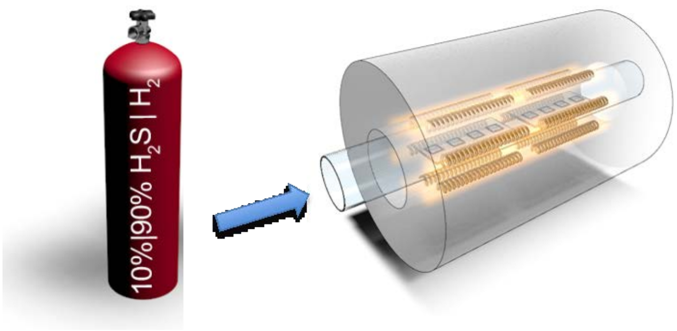
2. Surface Protection of CGSe with molybdenum disulphide – synthesis and characterization

a. Synthesize MoS_2 on CdS/CGSe





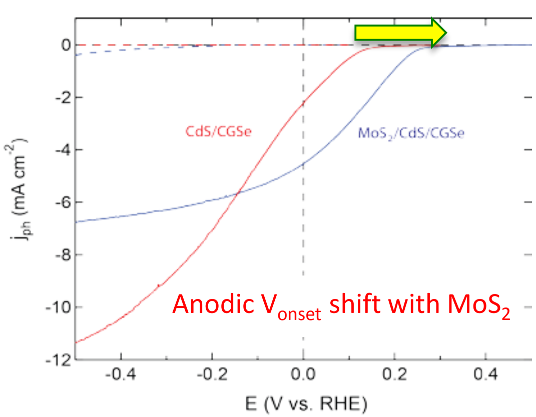
Step 1: Evaporate 5 nm of Mo
Step 2: Sulfurization in tube furnace at 200°C H_2S | H_2



2 nm MoS_2 shells have protected MoO_3 nanowires for 10,000 CVs

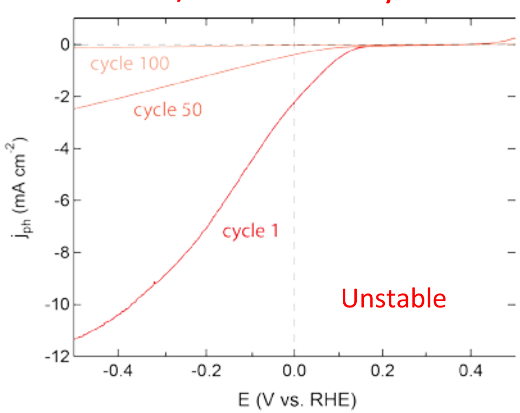
b. Activity and stability of MoS_2/CdS/CGSe in 0.5M H_2SO_4

Activity of MoS_2



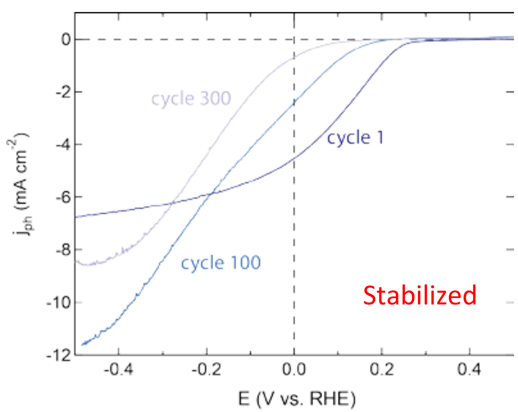
Anodic V_{onset} shift with MoS_2

CdS/CGSe stability test



Unstable

MoS_2/CdS/CGSe stability test

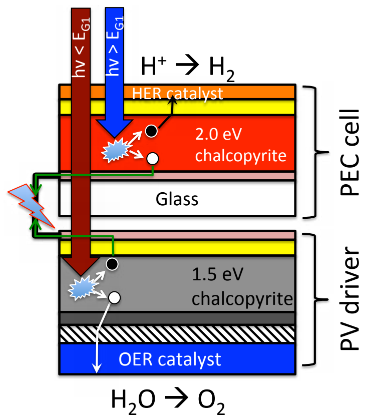


Stabilized

Take home messages:
- Suite of advanced characterization methods develop to understand corrosion mechanisms and test surface protection strategies,
- Formation of unstable Ga_2O_3 at chalcopyrite surface identify as a possible cause of photocorrosion,
- MoS_2 HER catalyst can effectively protect materials from degradation: MoO_3, Si, CdS…etc.

AG barriers

1. Simulation of the complete HPE system to identify solid-state requirements

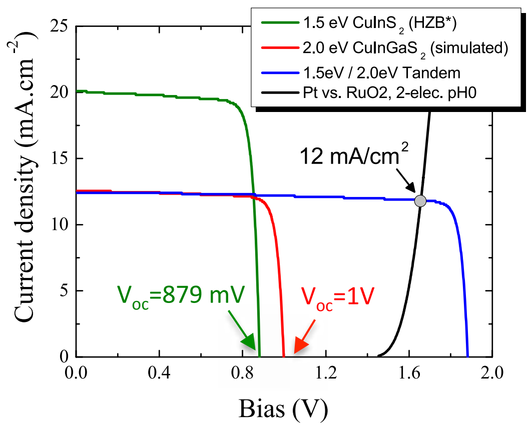


$V_{HPE}=V_{top}+V_{bottom}$

$J_{HPE}=\min(J_{top}, J_{bottom})$

Requirement for 15% STH (this program's goal):

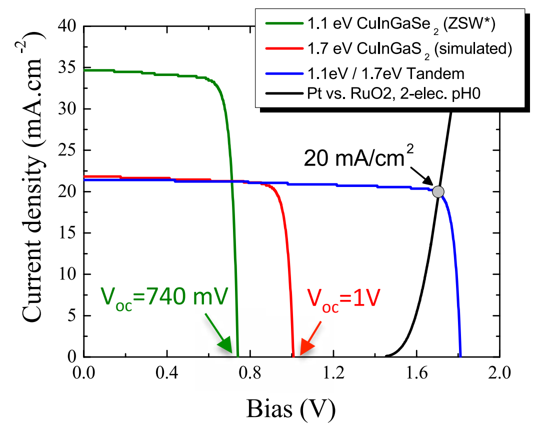
- Bottom cell: 1.5eV, V_{oc}= 879 mV (HBZ's CIS_2 cell)
- Top cell: 2.0eV, V_{oc}≈1.0 V, J_{sc}≈12-13 mA.cm^{-2}



* SOLARMAT 95, 864 (2011) / 879mV, 20 mA/cm2, FF: 70%, eff: 12.6%

Requirement for 25% STH (DoE's ultimate target):

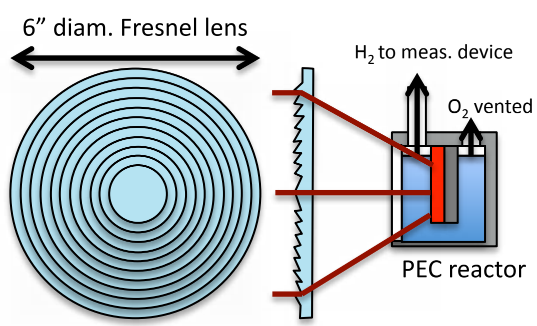
- Bottom cell: 1.1eV, V_{oc}=740 mV (ZSW's CIGSe cell)
- Top cell: 1.74eV, V_{oc}≈ 1.0 V, J_{sc}≈20-22 mA.cm^{-2}

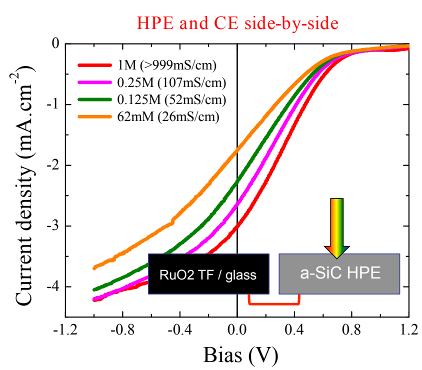


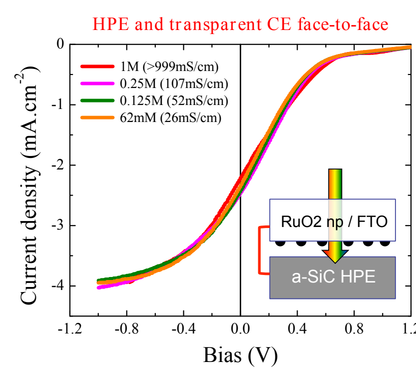
* Prog. Photovolt: Res. Appl. (2011) / 740mV, 35 mA/cm2, FF: 77%, eff: 20.3%

2. Outdoor testing using "Type 4" PEC reactor (10x concentrator + solar tracking)

→ Validate PEC reactor components (optics + encapsulation) and report STH efficiency of champion HPE devices







→ Alternative PEC reactor designs can reduce the need for highly concentrated acidic electrolytes

Collaborations

- US DoE PEC working group: white papers (metal oxides and chalcopyrites) and standardized test protocols,

- International Energy Agency/HIA/Annex 26: collaboration with international institutes and universities including the Institute for Solar fuels (HZB), Delft University, University of Warsaw (Poland)...etc,

- University of Louisville (M. Sunkara) / Jozef Stefan Institute-Slovenia (M. Mozetic): U.S./European project on physical vapor deposition of nanostructured PEC materials.

Project-specific collaborations:

- EMPA (A. Braun): in-situ characterization of phase transformation during CIGS synthesis (**TASK 1**),

- Columbia (D. Esposito): spatially resolved UV-vis analysis on composition graded chalcopyrites (**TASK 1**),

- University of Los Andes-Colombia (S. Barney): reactive sputtering of ZnOS buffers (**TASK 2**),

- AIST-Japan: provide narrow bandgap CIGSe PV drivers (supported by METI-DoE clean energy plan) (**TASK 4**),

- University of Bordeaux-France (A. Rougier): development of temperature-resistant TCOs as intermediate layers for multi-junction CIGSSe solar cells and PEC devices (**TASK 4**),

- UC-Irvine (S. Ardo): Faradaic efficiency measurement on wide bandgap CIGS systems (**TASK 4**).

Remaining challenges & barriers / Proposed future work

Task 1. PV-grade wide bandgap Cu(In,Ga)S_2 absorbers

Challenges/Barriers: controlling elemental composition profile in PV-grade 1.8-2.0eV CIGS.

Proposed Future Work: evaluate the impact of sulfurization annealing process (RTP vs. slow ramp, sulfur pressure) on gallium and indium profile, supported by theory and advanced characterization teams.

Task 2. Sub-surface energetics improvement (p/n junction)

Challenges/Barriers: free electron losses (Eg-Voc) appear to be greater with sulfide than selenides.

Proposed Future Work: with input from the theory team, we will evaluate post deposition treatments (naF, KF) to passivate surface defects and develop alternative buffer layers. CIGS/buffer interface will be characterized at UNLV.

Task 3. Surface catalysis and corrosion resistance

Challenges/Barriers: coating a pin-hole free 5nm-thick MoS_2 layer on a rough polycrystalline CIGSSe film is challenging.

Proposed Future Work: we will replace our current MoS_2 deposition process (Mo evaporation followed by H_2S sulfurization) with highly conformal deposition techniques, including MOCVD and ALD, and measure durability of our MoS_2-coated PEC materials.

Task 4. Device certification and efficiency benchmarking

Challenges/Barriers: achieving STH efficiency > 15% requires minimal electrical, kinetic and optical losses throughout the device.

Proposed Future Work: we will perform a complete loss analysis of our proposed HPE device, identify weaknesses and explore path for optimization.

Project summary

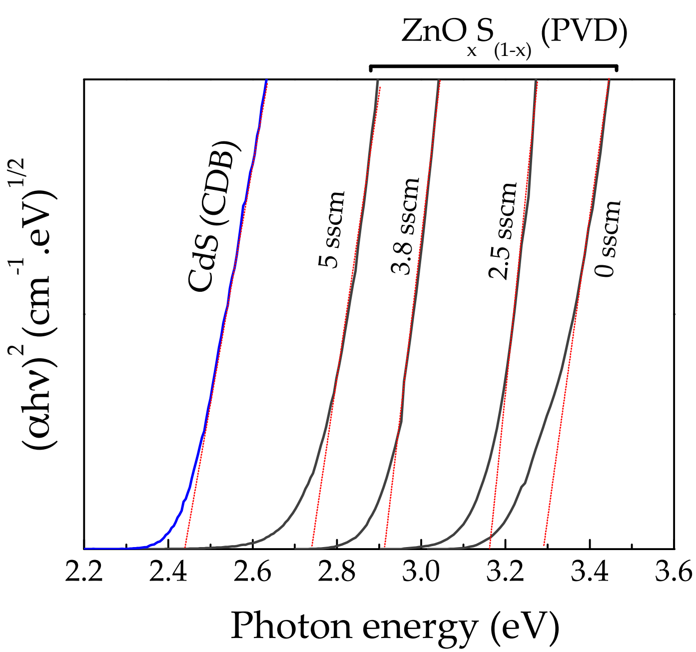
Relevance	Create the first all-chalcopyrite HPE device with low-cost, PV-grade and durable thin film materials to meet DoE's efficiency and durability targets.
Approach	Focus on the development of wide bandgap chalcopyrite PEC materials, identify compatible buffers to improve energetics (p-n junction), evaluate Earth-abundant MoS_2 as both HER and protection layer and assess the STH efficiency of the complete HPE device.
Accomplishments	(1) Identified 3 chalcopyrite material systems with optimum optical properties for PEC H_2 production, (2) successfully fabricated PV-grade 1.55eV CIGS absorbers generating 13 mA/cm^2 (in both PV & PEC integration), (3) demonstrated the crucial role of the CdS buffer on HER turn on voltage and identified alternative buffer materials for wide E_G chalcopyrites, (4) developed new in-situ advanced characterization methods to elucidate photocorrosion and tested MoS_2 as a protective layer and (5) established solid-state requirements for both bottom and top cells in order to meet DoE's short (15%) and long (25%) term goals.
Collaborations	Project-specific collaboration with U.S. and international teams to address barriers in each of the 4 technical tasks.
Proposed future work	(1) Continue development of PV-grade and demonstrate at least 10-12 mA/cm2 with 1.8eV CIGS (FY15 Go/NoGo), (2) fabricate, characterize and test ZnOS as an alternative buffer and demonstrate Voc > 750 mV (FY16 Go/NoGo), (3) continue development of conformal MoS_2 coating using ALD or MOCVD processes to meet 500 (FY15), 750 (FY16) and 1,000 (FY17) hour durability targets and (4) validate the 1.5eV/2.0eV HPE structure and measure its STH efficiency.

Technical back-up slides

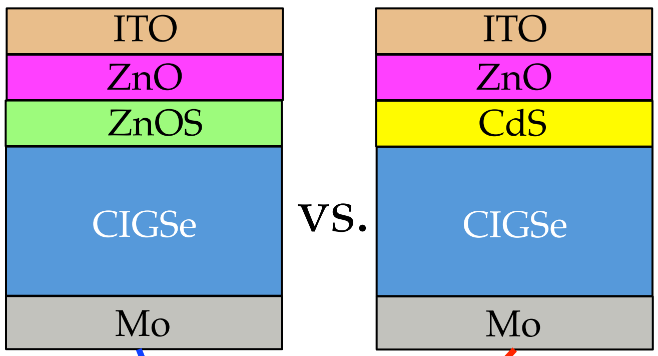
HNEI – University of Los Andes collaboration on ZnOS buffers

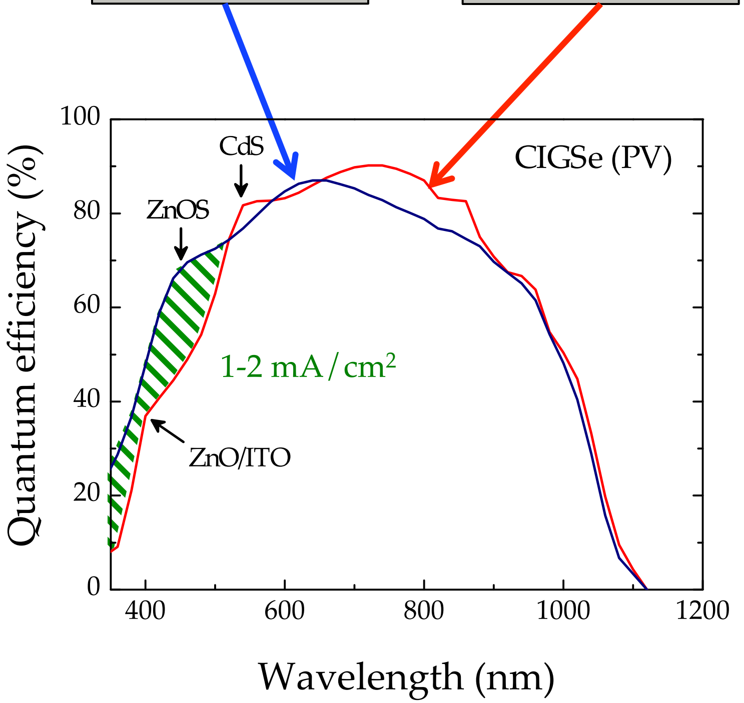
Non-toxic n-type buffer: ZnOS

- → Reactive sputtering using ZnS target
- → Optical absorption controlled with O_2 pp
- → 2.7 eV ZnOS transmits more light than CdS: ↗ Jsc
- → Buffer (ZnOS) & HER catalyst (Ru) deposited back to back



CIGSe (1.1 eV) PV integration schemes

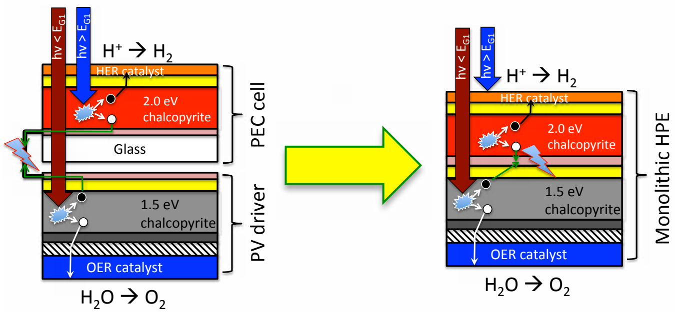




→ Successful synthesis of bandgap tunable ZnOS n-type buffers

HNEI – University of Bordeaux collaboration on temperature-resistant TCOs

Barrier: temperature-resistant TCO are required for CIGSe/CIGS PV/PEC devices monolithic integration



Solar Energy Materials & Solar Cells 127 (2014) 174–178

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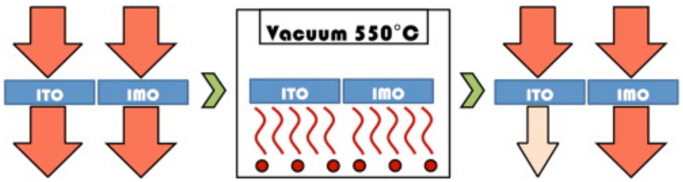
journal homepage: www.elsevier.com/locate/solmat

Temperature-resistant high-infrared transmittance indium molybdenum oxide thin films as an intermediate window layer for multi-junction photovoltaics

Alexander D. DeAngelis [a,*], Aline Rougier [b], Jean-Pierre Manaud [b], Christine Labrugère [c], Eric L. Miller [d], Nicolas Gaillard [a]

[a] Hawaii Natural Energy Institute, University of Hawaii, Honolulu, HI 96822, USA
[b] CNRS, Univ. Bordeaux, ICMCB, UPR 9048, F-33600 Pessac, France
[c] CeCaMA, Univ. Bordeaux, ICMCB, UPR 9048, F-33600 Pessac, France
[d] US Department of Energy, Washington, DC 20585, USA

1. Experimental



2. Resistivity measurements

Table 1
Electrical properties measured via the Van der Pauw method showing.

	Sheet resistance R_s (Ω/sq) ±0.15	Resistivity ρ (Ω-cm) $\pm 0.02 \times 10^{-4}$
ITO unannealed	52.16	5.22×10^{-4}
ITO annealed	28.37	2.84×10^{-4}
IMO unannealed	300.31	3.00×10^{-3}
IMO annealed	49.48	4.95×10^{-4}

→ IMO and ITO have comparable resistivity after annealing

3. UV-visible measurements

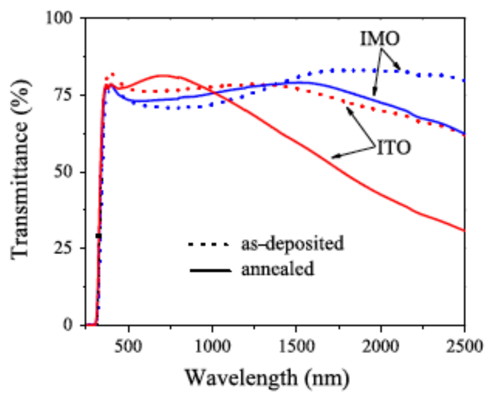
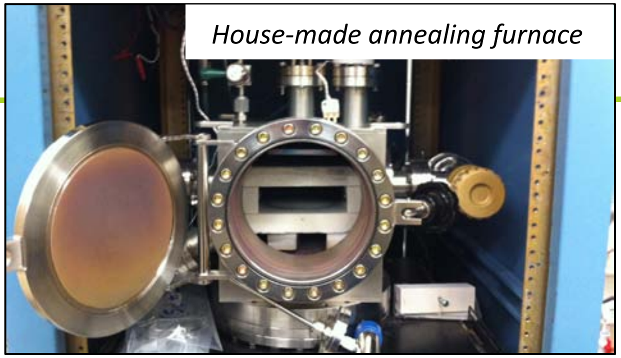


Fig. 1. Optical transmittance of typical IMO and ITO samples measured from 250 to 2500 nm. Infrared transmittance of IMO remains high even after annealing whereas that of ITO has decreased significantly.

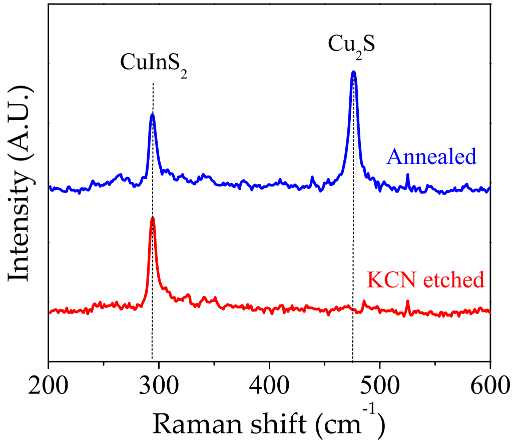
→ Annealed IMO is more transparent than as-deposited ITO!

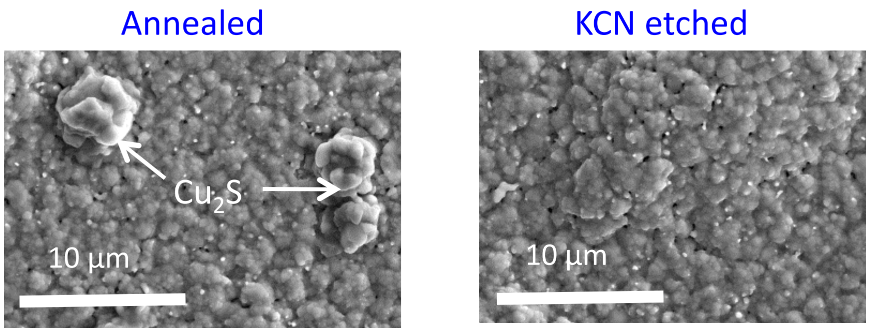
→ IMO identified as candidate TCO for CIGSe/CIGS monolithic HPE integration

New thin film synthesis process for PV-grade CIGS

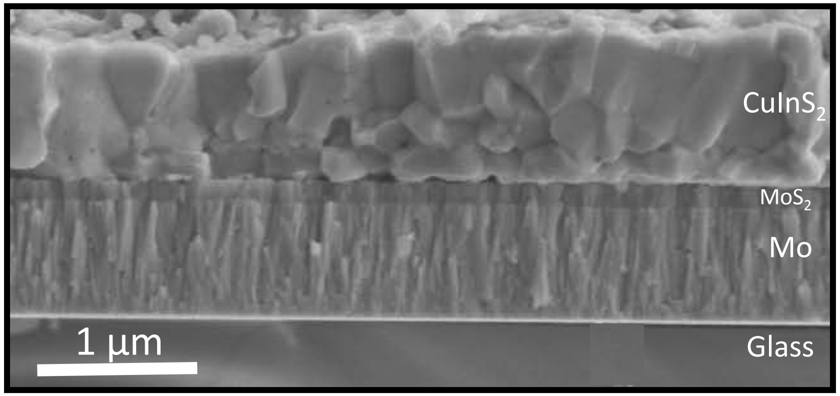


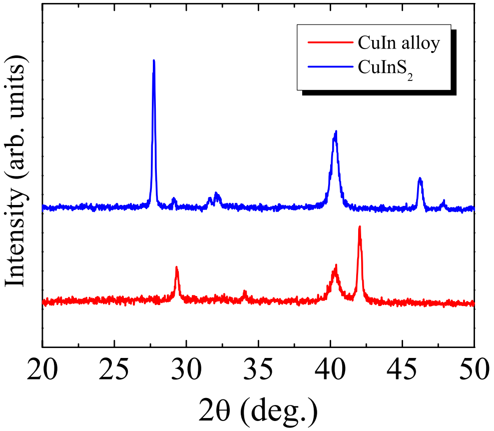
1. Cu-In-Ga alloy deposition by co-evaporation with copper in excess
2. Sample & sulfur placed in petri dish or graphite box
3. Annealing under controlled back-ground pressure (450-525°C)





"Self adjusting" stoichiometry

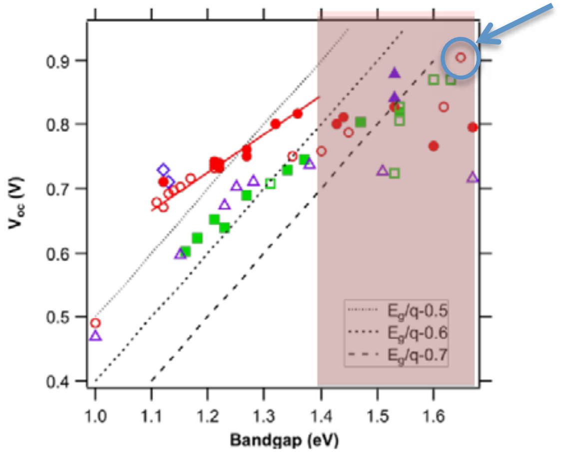




→ CIGS films with improved morphology and microstructure successfully fabricated

Reported PV-grade "intermediate bandgap"CIGSe and "wide bandgap" CIGS

a. CIGSe (NREL)



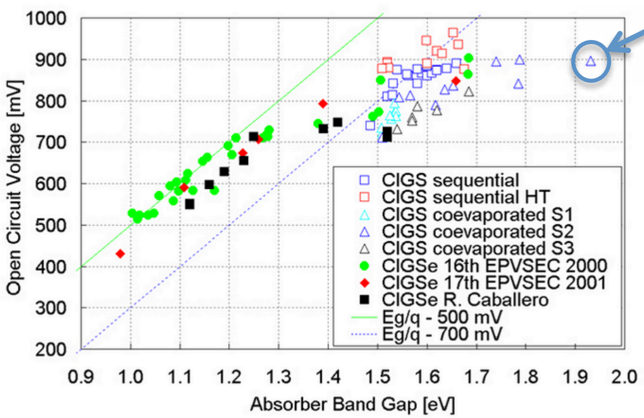
910mV Voc reported with 1.67eV $CGSe_2$

Miguel Contreras, Lorelle Mansfield, Brian Egaas, Jian Li, Manuel Romero, and Rommel Noufi
National Renewable Energy Laboratory

Eveline Rudiger-Voigt and Wolfgang Mannstadt
Schott AG

Presented at the 37th IEEE Photovoltaic Specialists Conference (PVSC 37)
Seattle, Washington
June 19-24, 2011

b. CIGS (HZB)



895mV Voc reported with 1.95eV $CIGS_2$

R. Klenk, J. Klaer, C. Köble, M. Lux-Steiner, R. Mainz, S. Merdes, H. Rodriguez-Alvarez, R. Scheer and H. Schock. Development of CuInS2-based solar cells and modules. Solar Energy Materials Solar Cells 95, 1441-1445 (2011), doi: 10.1016/j.solmat.2010.11.001.