

Wide Bandgap Chalcopyrite Photoelectrodes for Direct Solar Water Splitting

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Hawaii Natural Energy Institute

2016 DoE Annual Merit Review

June 8th 2015

Project ID#: PD116

Overview

Timeline

- Project start date: 10/1/2014
- Passed GNG#1: 10/6/2015
- Project end date: 9/30/2017

Budget

- Total budget funding: \$3,050,000
 - DoE share: 100%
 - Contractor share: 0%
- Total DoE funds spent as of 03/2016 (including Nat. Labs): \$1,250,000

Barriers

Challenges for PEC H2 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 PEC team (K. Zhu, T. Deutsch, J. Turner)**
 - Device validation and PEC reactor design
- **NREL CIGS group (M. Contreras)**
 - New chalcopyrites and buffers

Relevance - Objectives

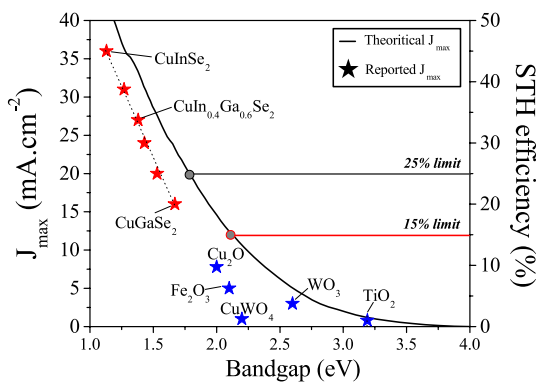
- **Long-term goal:** identify efficient and durable copper chalcopyrite-based materials which can operate under moderate solar concentration and capable of generating hydrogen via PEC water splitting at a cost of \$2/kg or less.

- **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 H₂ under 10x concentration (“Type 4” PEC reactor) in 8 hours.

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-TPDH 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

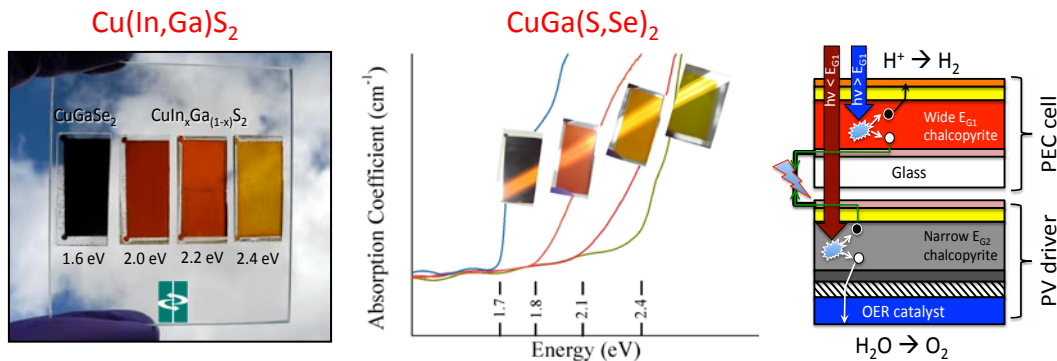
Relevance – Benefits of copper chalcopyrites for PEC H2 production

1. PV-grade materials



Photocurrent densities in line with DoE targets

2. Bandgap tunable

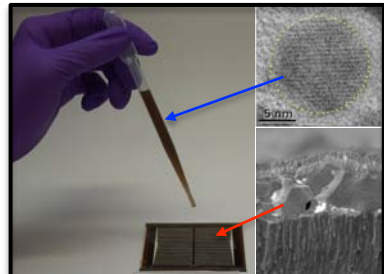


PV driver and PEC electrode can be stacked for efficient PEC H2 production

3. Cost-effective processes developed

Production

R&D

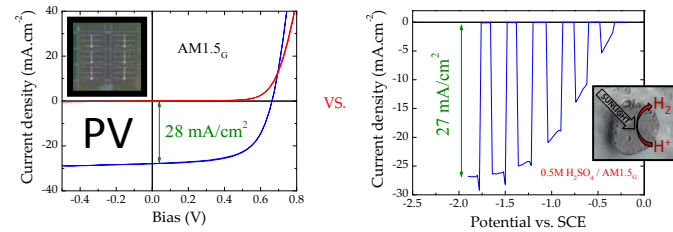


Solution processed chalcogenide material (ONR funding)

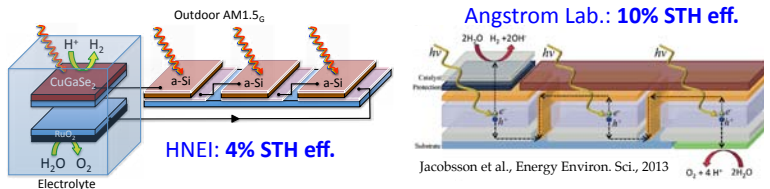
The CIGSse class can meet DoE's material target cost of \$60/m².

4. Efficient PEC water splitting demonstrated with CIGSSe

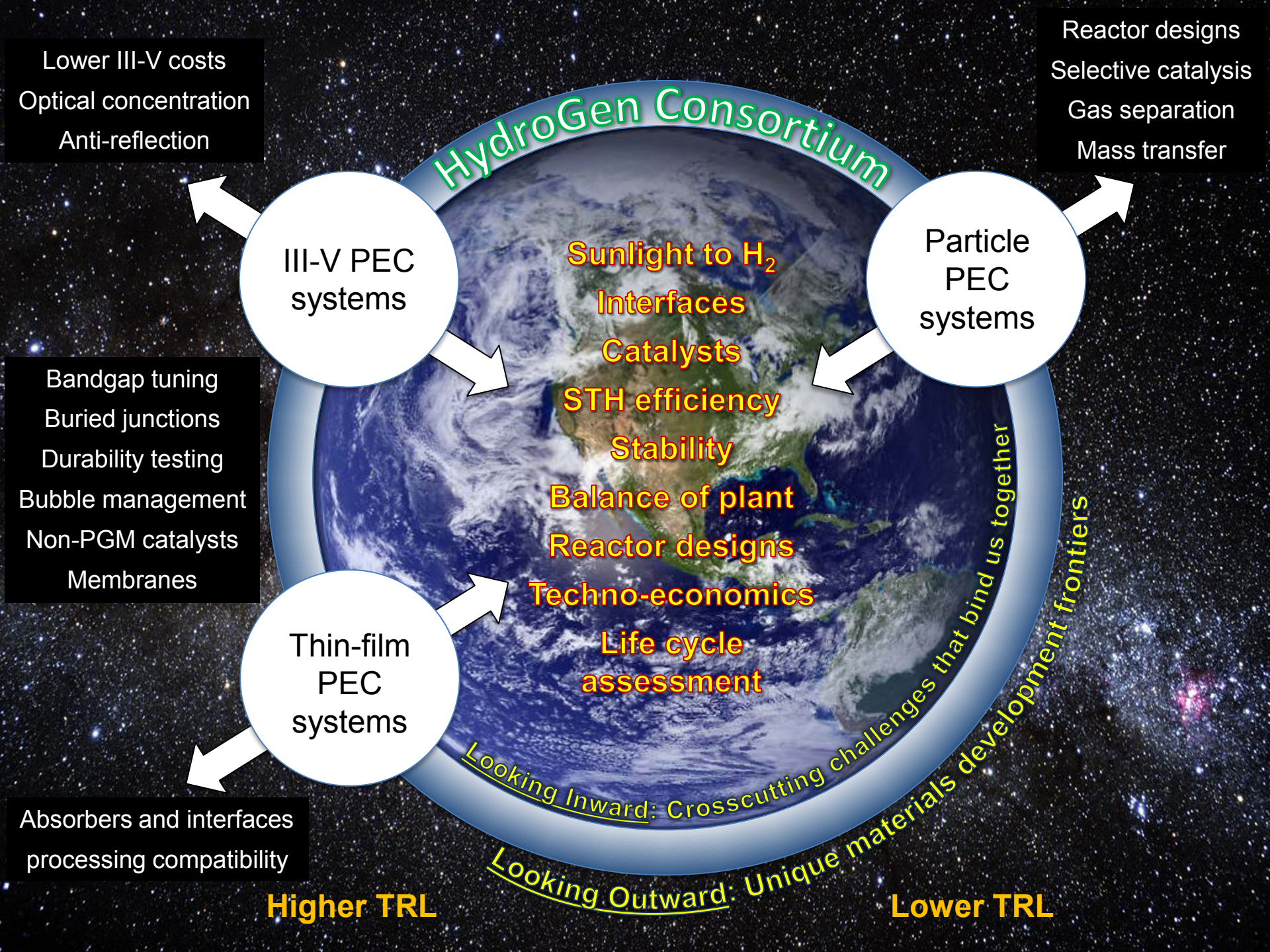
Electrodes



Devices



Take home message: copper chalcopyrites (CuInGaSe₂) are excellent candidates for PEC water splitting. New materials with wider bandgaps are needed to relocate PV driver(s) under the photocathode (HPE structure) in order to achieve STH efficiencies >10%.



HydroGen Consortium

III-V PEC systems

- Lower III-V costs
- Optical concentration
- Anti-reflection

Particle PEC systems

- Reactor designs
- Selective catalysis
- Gas separation
- Mass transfer

Thin-film PEC systems

- Bandgap tuning
- Buried junctions
- Durability testing
- Bubble management
- Non-PGM catalysts
- Membranes

- Sunlight to H₂
- Interfaces
- Catalysts
- STH efficiency
- Stability
- Balance of plant
- Reactor designs
- Techno-economics
- Life cycle assessment

Looking Inward: Crosscutting challenges that bind us together

Looking Outward: Unique materials development frontiers

Higher TRL

Lower TRL

- Absorbers and interfaces
- processing compatibility

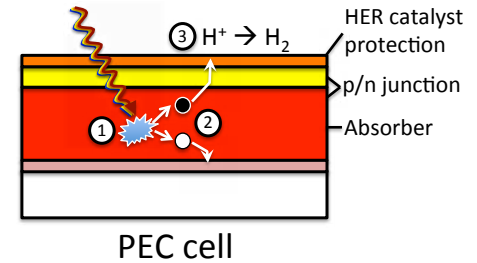
Approach – Milestones

Task 1. PV-grade wide bandgap Cu(In,Ga)S₂ absorbers: **AE and AJ barriers**

Task 2. Sub-surface energetics improvement (p/n junction): **AE and AG barriers**

Task 3. Surface catalysis and corrosion resistance: **AE and AF barriers**

Task 4. Device certification and efficiency benchmarking: **AG barrier**



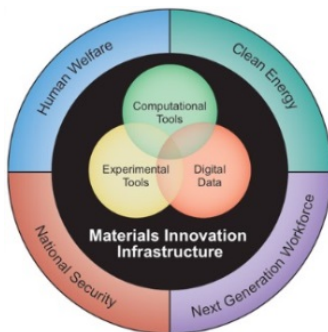
Task#	FY15 Milestones	Due Date	Status
1	Synthesize a CuInGaS ₂ thin film material with controlled stoichiometry & microstructure	12/2014	Complete
2	Fabricate Cu(In,Ga)S ₂ cells with Voc > 600 mV	03/2015	Complete
3	Durability > 500 hrs at 8 mA/cm ² with a chalcopyrite photoelectrode	06/2015	25%
4	Chalcopyrite photoelectrode with bandgap > 1.7eV that generates at least 10-12 mA/cm ²	09/2015	Complete
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/cm²			

Task#	FY16 Milestones	Due Date	Status
1	Cu(In,Ga)S ₂ solar cells with a photoconversion efficiency > 6%	12/2015	Complete
4	Photocurrent density relevant to 15-16% STH with chalcopyrite 12-13 mA/cm ²	03/2016	90%
3	Durability > 750 hrs at 8 mA/cm ² , with a stretch goal of 1,000 hrs	06/2016	30%
2	Fabricate Cu(In,Ga)S ₂ cells with Voc > 750 mV	09/2016	95%
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	Due Date	Status
1	Photocurrent density relevant to 16-17% STH with a chalcopyrite 13-14 mA/cm ²	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% generating at least 3L of H ₂ in 8 hrs.	09/2017	

Approach – Integrating experiment, computation and theory

Materials Genome initiative (MGI) / Energy Materials Network (EMN)



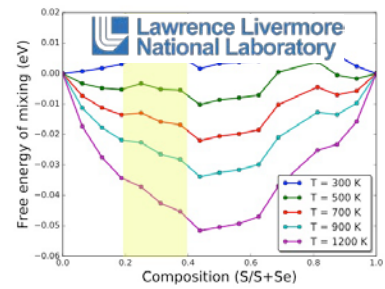
Innovative materials discovery and development for faster product development. Key elements include:

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

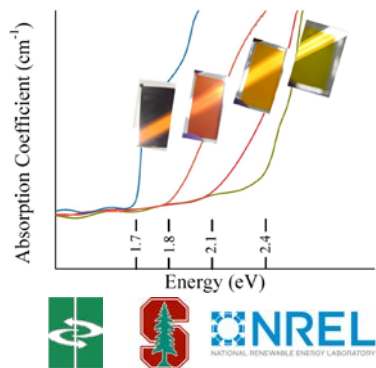
Accelerating materials development using integrated modeling, synthesis and advanced characterizations:

1. New wide bandgap materials discovery using theoretical modeling: bandgap, conductivity type and defect density.
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.

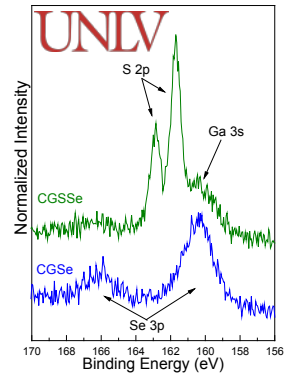
Modeling



Synthesis

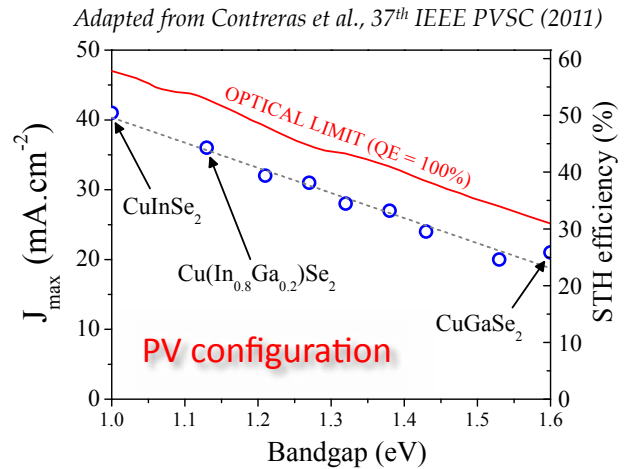
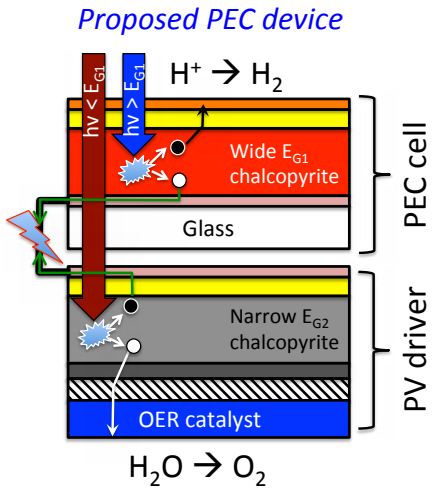


Advanced analysis

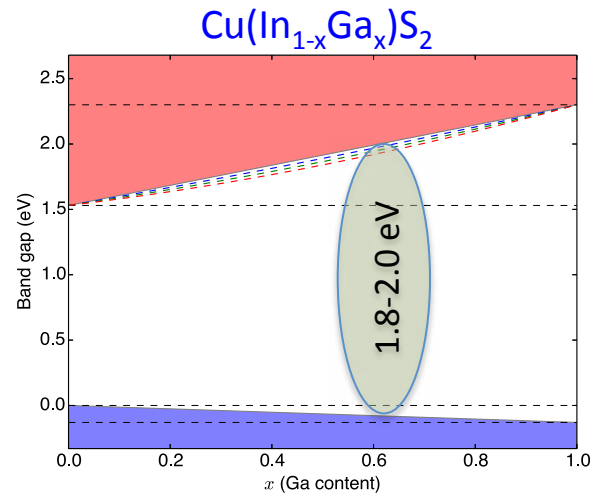


Accomplishments – Task 1: PV-grade absorbers

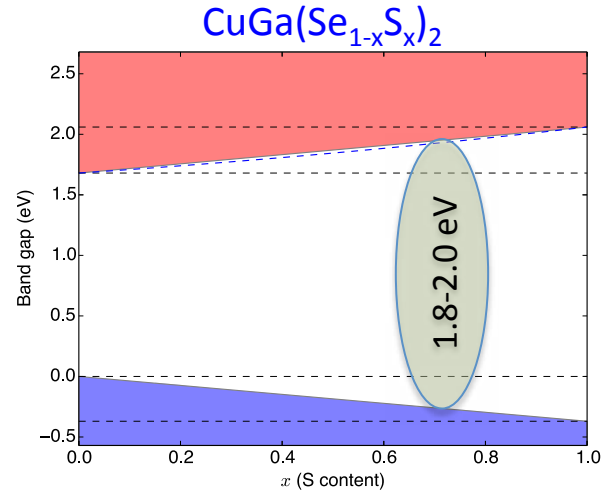
1. Identifying chalcopyrite material candidates with $1.8 \text{ eV} < E_g < 2.0 \text{ eV}$



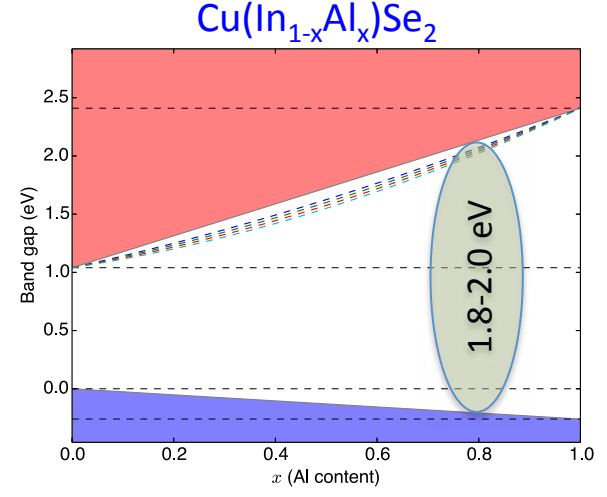
- PEC device: all-chalcopyrite dual absorber HPE,
- CIGSe ideal PV driver, but E_g too narrow for PEC,
- Absorbers with $1.7\text{eV} < E_g < 2.0\text{eV}$ required.



Proposed method: post dep. annealing



Proposed method: post dep. annealing



Proposed method: direct co-evaporation

→ 3 alloys with great potential for PEC applications identified : $\text{CuIn}_{0.4}\text{Ga}_{0.6}\text{S}_2$ (AMR 2015), $\text{CuGaSe}_{0.7}\text{S}_{0.3}$ (today's presentation) & $\text{CuIn}_{0.2}\text{Al}_{0.8}\text{Se}_2$.

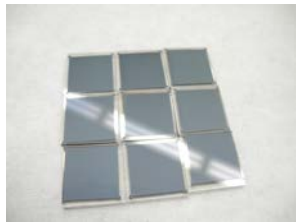
2. Development of bandgap tunable CuGa(S,Se) absorbers

a. Materials development and testing

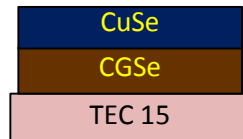
Synthesis:

Step 1: co-evaporated CuGaSe/CuSe stacks

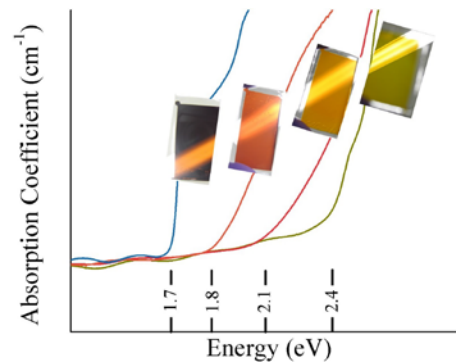
Step 2: annealing with controlled amount of sulfur



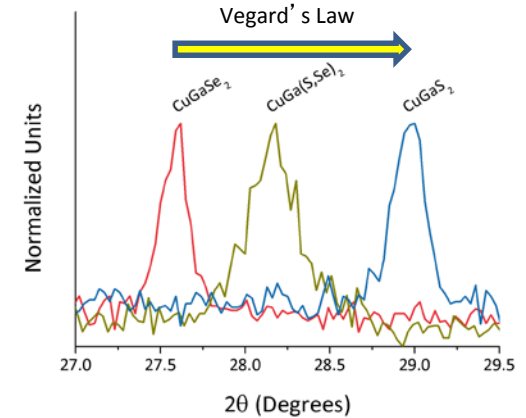
As deposited CuGaSe/CuSe precursors



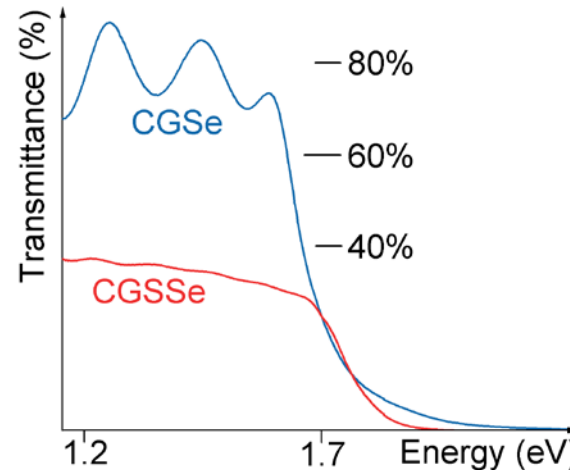
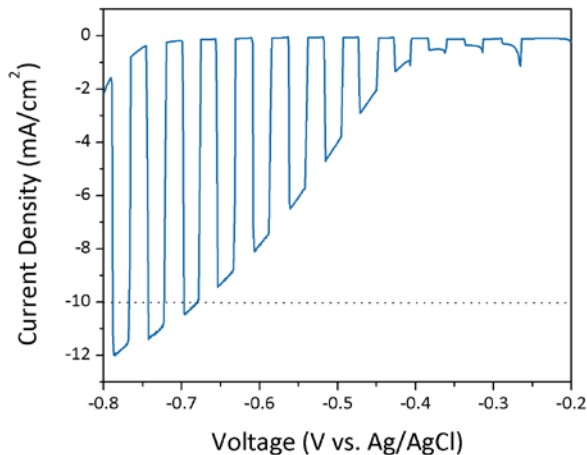
Bandgap tunable CuGa(S,Se)₂



Bulk phase transformation with addition of sulfur to CGSe



LSV measurement of CGSSe (1.75 eV, 1.9 μm)



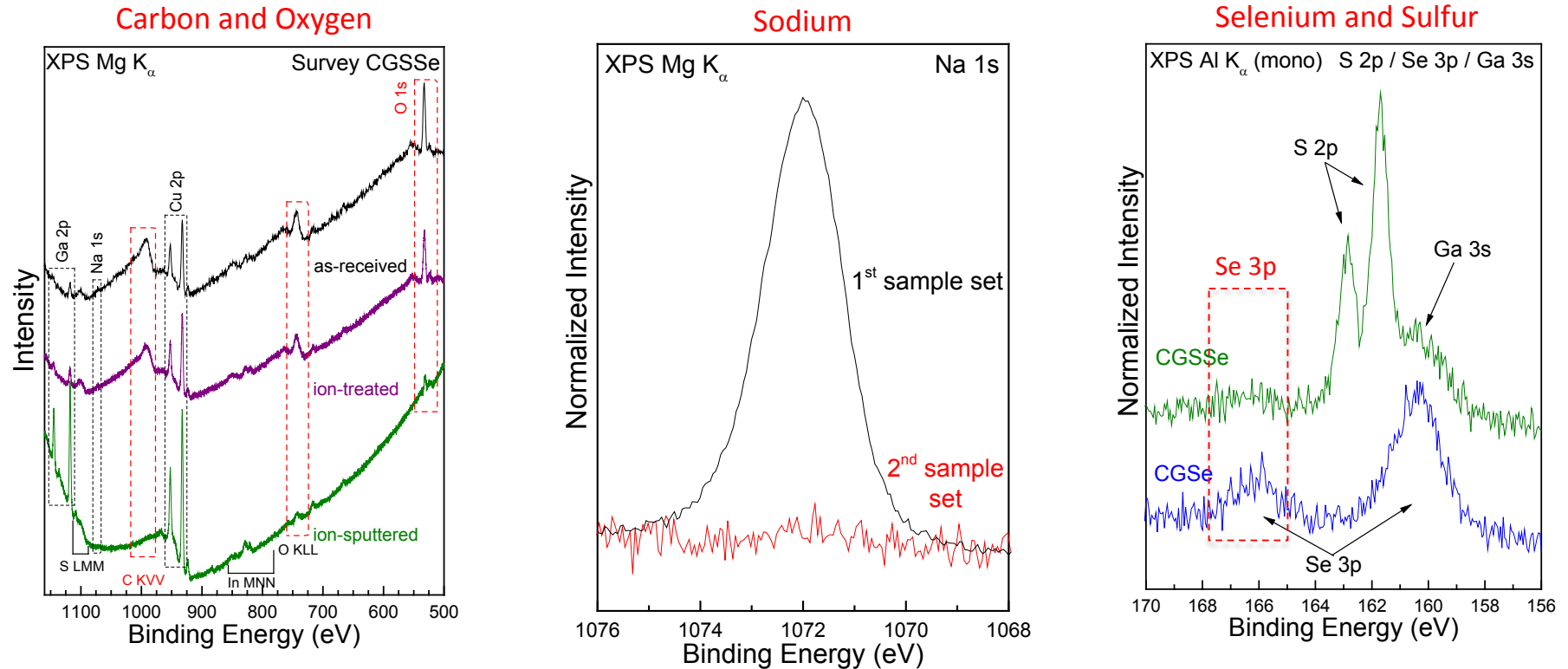
→ Bandgap tunable single phase CuGa(S,Se) absorbers successfully fabricated,

→ Photocurrent density over 10 mA/cm² achieved with 1.75 eV CGSSe (GNG #1),

→ When compared to CGSe, CGSSe has a lower sub-bandgap transmission

2. Development of bandgap tunable CuGa(S,Se) absorbers

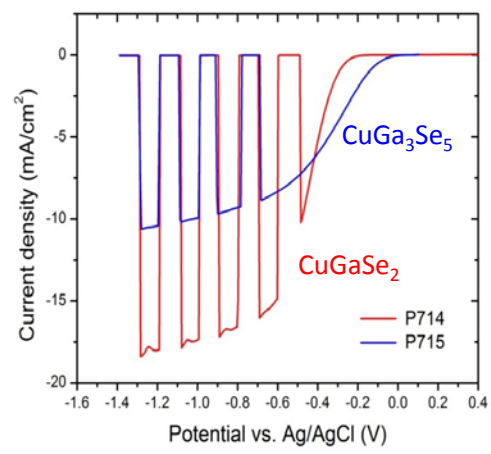
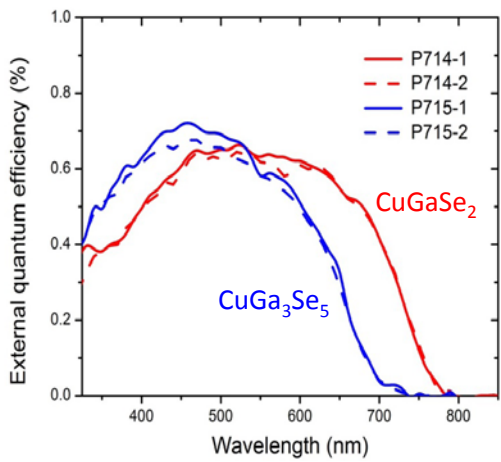
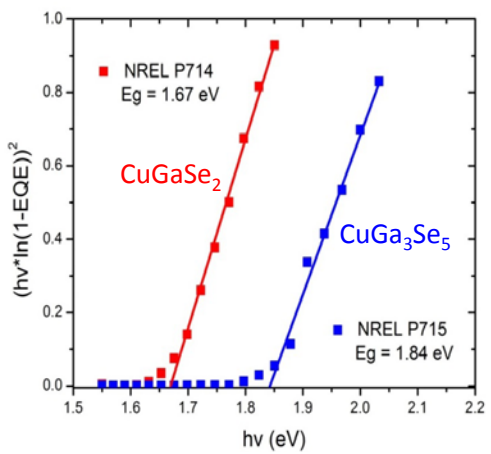
b. Identifying possible impurities in CuGa(S,Se)₂ by XPS (UNLV)



- As deposited samples: significant presence of carbon and oxygen at the surface,
- After “surface cleaning” (ion treatment): no carbon in the bulk (within sensitivity of C KLL line), but O still present,
- Gained control of Na surface impurities between 1st and 2nd sample set: improved annealing process
- Gained insight into sulfurization behavior

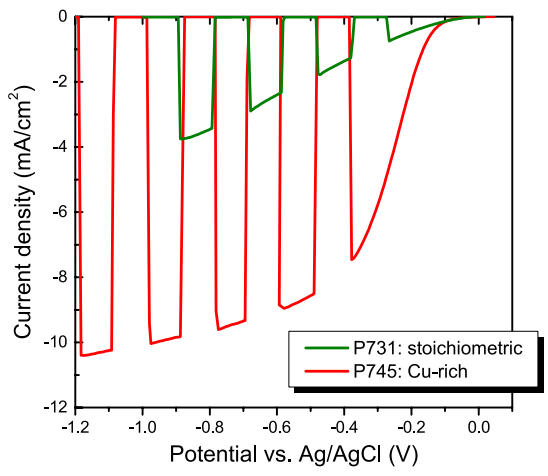
3. Ordered defect CuGa₃Se₅ absorbers (NREL)

a. Initial results on CuGa₃Se₅, compared with CuGaSe₂



b. CuGa₃Se₅ composition optimization

	Cu/Ga	E _g (eV)	J (mA/cm ²)	
TARGET	0.33			
P731	0.3311	1.83	4	Stoichio.
P732	0.3389	1.85	5	
P740	0.3535	1.84	10	Cu-rich
P742	0.3569	1.85	10	
P715	0.3603	1.84	10	
P745	0.3788	1.85	10	
P746	0.3904	1.81	11	



- Bandgap constant for a wide range of Cu content
- Lower bandgap leads to higher current density
- Excess Cu seems beneficial for PEC

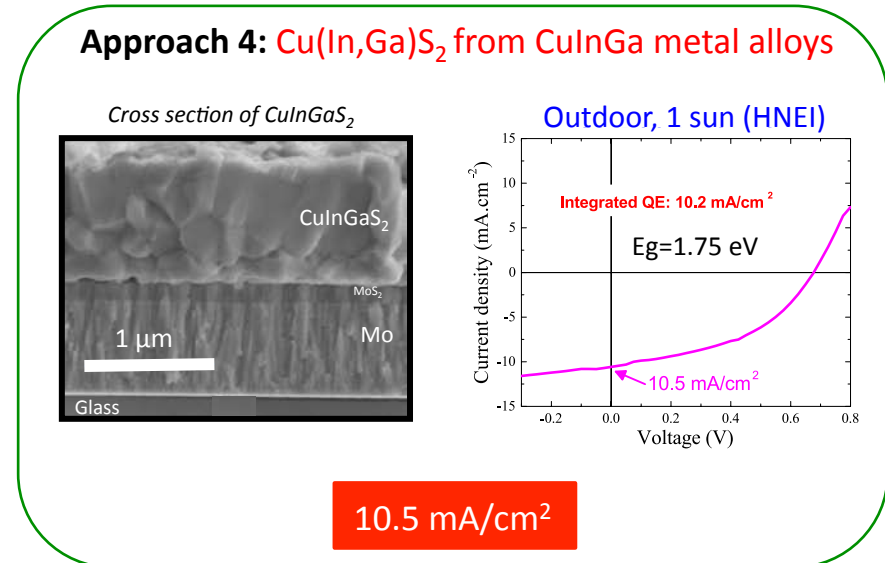
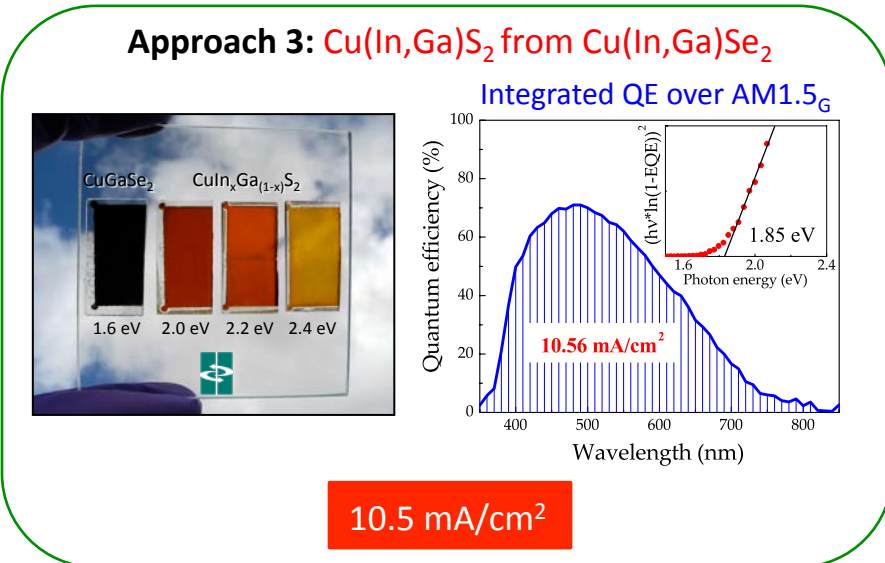
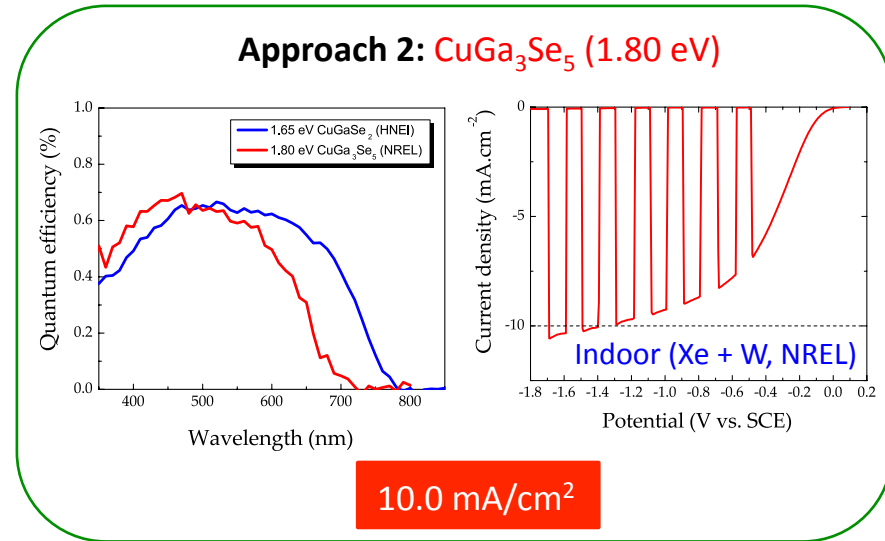
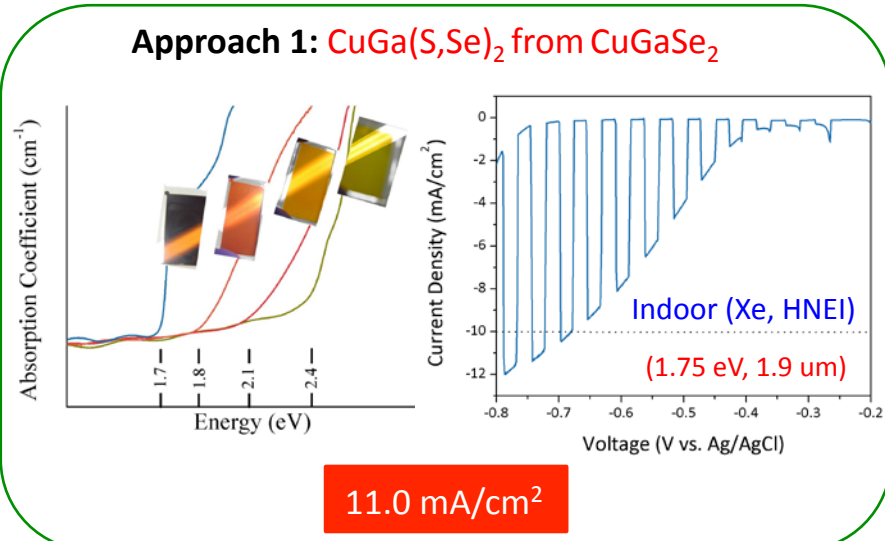
→ What is the role of Cu? Cu poor is preferred for CIGS PV absorber, but not for CuGa₃Se₅

→ Can we adjust composition to obtain 1.7–1.8 eV absorber without secondary phase?

Accomplishments – Task 1: PV-grade absorbers

AE / AJ barriers

Summary for year 1: 4 approaches successfully met GNG #1 ($E_g > 1.7\text{eV}$ with $J > 10\text{mA/cm}^2$)

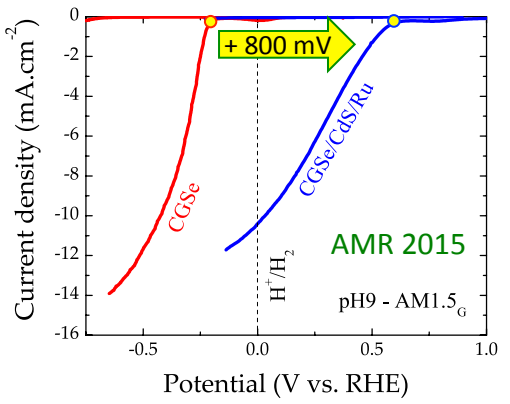


Accomplishments – Task 2: Sub-surface energetics

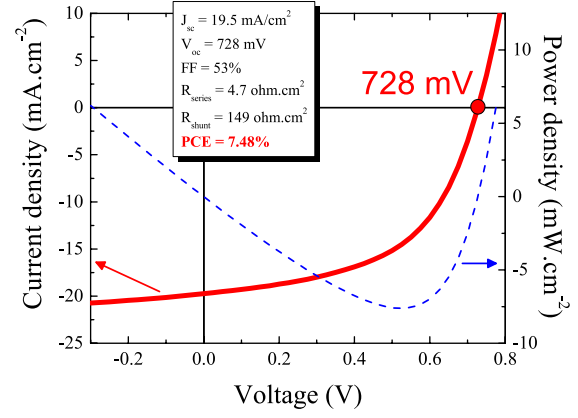
AE / AG barriers

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

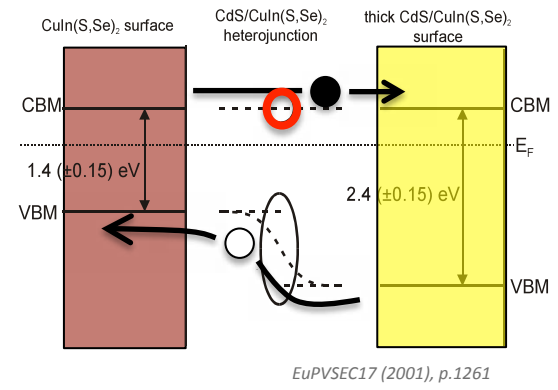
PEC: CGSe + CdS + Ru n.p. (HER catalyst)



PV: CIGS₂ + CdS + ZnO/ITO

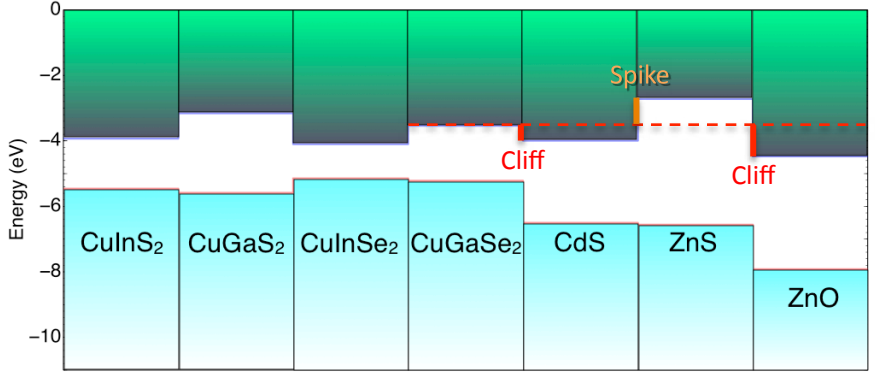


Band alignment @ CuIn(S,Se)₂/CdS interface

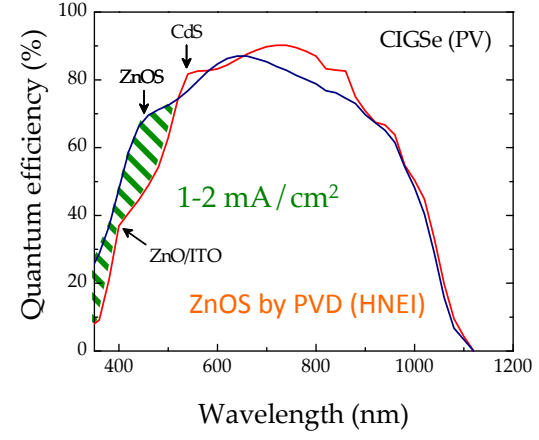


2. Development of new buffers for wide Eg chalcopyrites

Theoretical modeling of band offsets



Effect of buffer Eg on PV cell J_{sc}



ZnOS CBD process

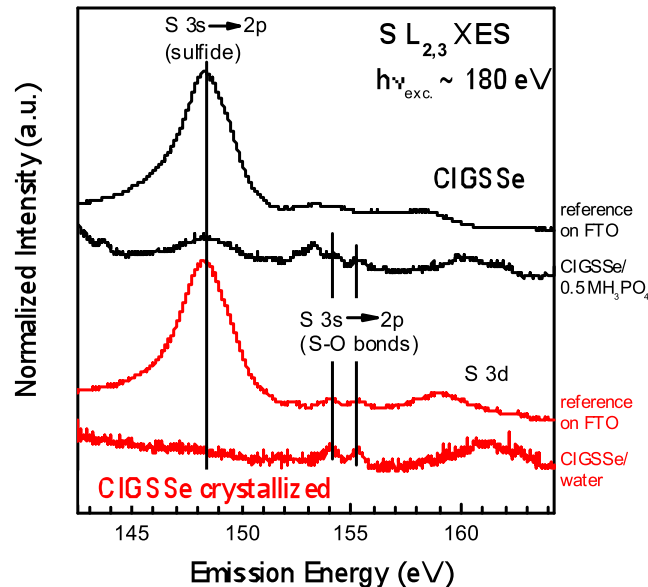
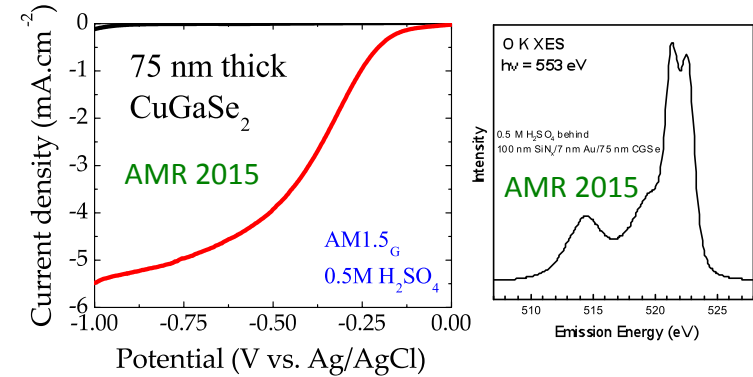
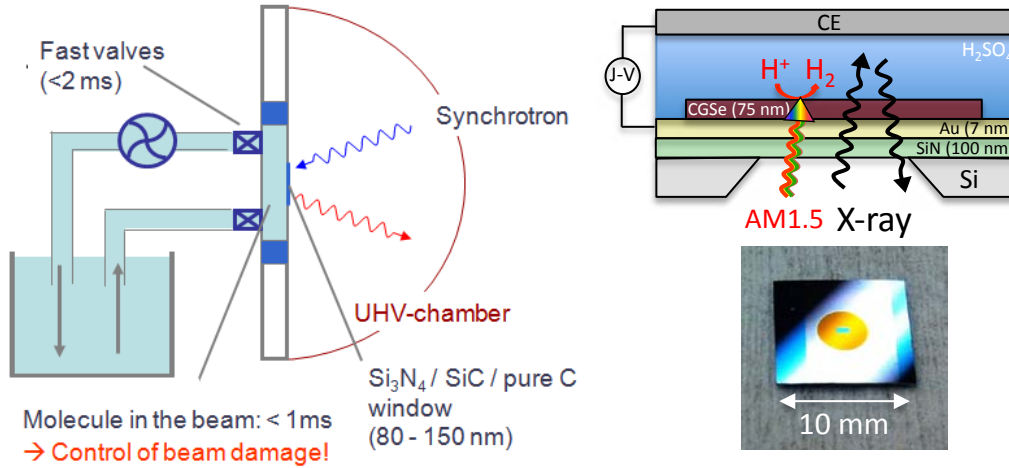


ZnOS identified by theory → on-going optimization HNEI with NREL's CIGS team support

Accomplishments – Task 3: Surface catalysis/corrosion resistance

1. Assessing the origin of chalcopyrite photocorrosion

In-situ soft X-ray Emission Spectroscopy of the CIGSSe/electrolyte interface



- First S L_{2,3} XES solid/liquid interface measurements of a PEC material:

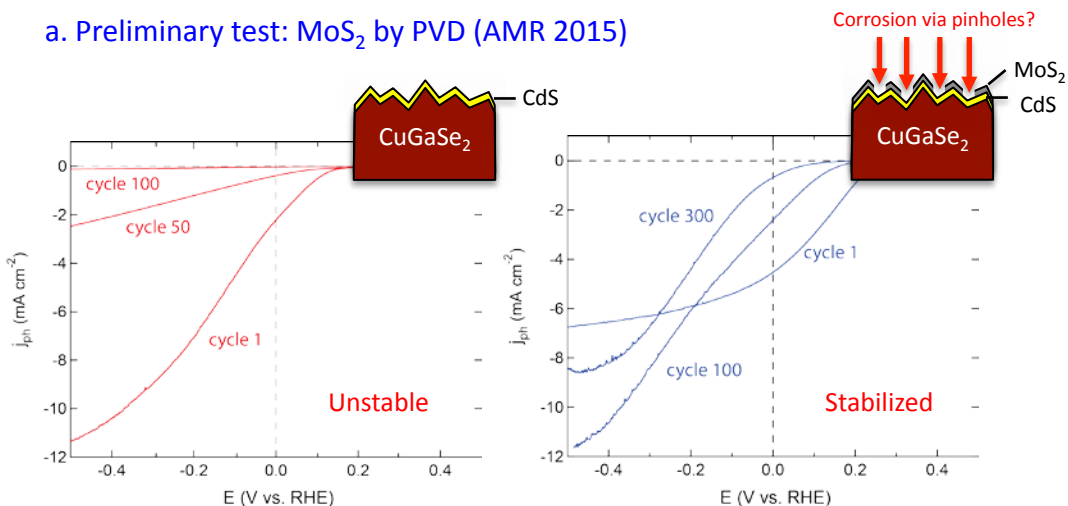
- Amorphous CIGSSe/0.5 M H₃PO₄
- Crystallized CIGSSe/water

Complex interplay of sulfide species and different oxidized sulfur environments, in particular sulfate:

→ Possible oxygen diffusion from FTO substrate?

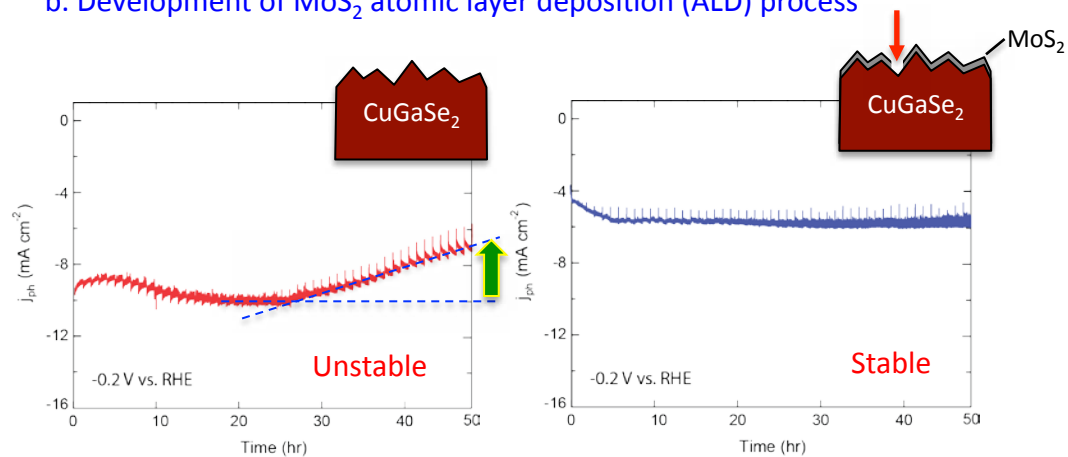
2. Protecting chalcopyrites against photocorrosion using MoS₂ or TiO₂

a. Preliminary test: MoS₂ by PVD (AMR 2015)



- MoS₂ PVD deposition not conformal on rough CGSe₂: pinholes
- Note: 600 hours durability achieved MoS₂ PVD on atomically flat Si (PD119)

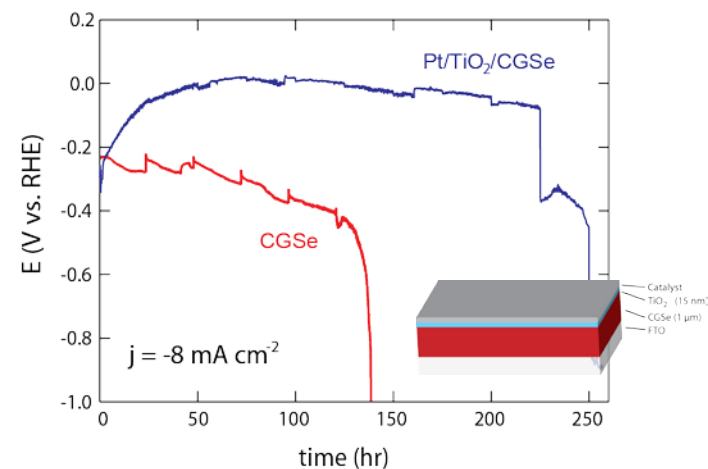
b. Development of MoS₂ atomic layer deposition (ALD) process



→ Improved durability with MoS₂ deposited by ALD : optimization on-going

c. Protection with well-established TiO₂ ALD coatings

→ 15nm thick TiO₂ layer deposited by ALD on CGSe₂

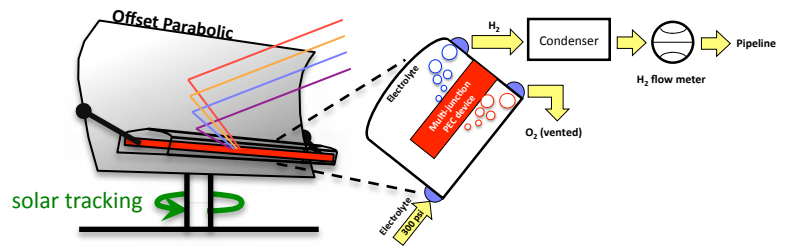


TiO₂ film doubled lifetime of CGSe electrodes (125 hrs to 250 hrs) but provides incomplete barrier against degradation

Future work on corrosion protection:

- Better understand chalcopyrite corrosion mechanisms,
- Quantify microscopic defects (pinholes) in protective layers,
- Identify failure mechanisms,
- Extend corrosion protection resistance to 1,000 hours.

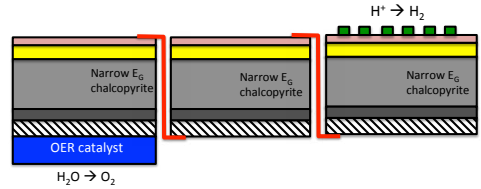
Accomplishments – Task 4: updated TEA on CIGS-based PEC systems



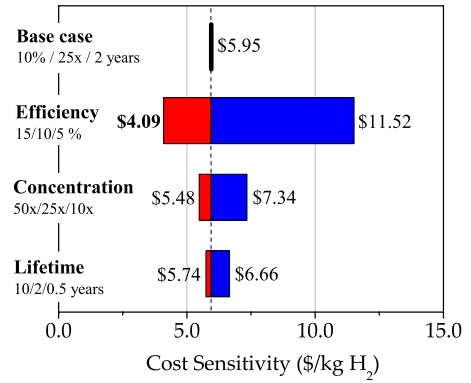
- H2A model parameters:**
- 50 TPD centralized plan (H2A on a 2 TPD sub-plan),
 - Operating capacity: 98%,
 - “Type 4” PEC reactor,
 - Reactor + optics (25x base case) replaced every 10 yrs.

Current technology (2012)

Co-planar architecture

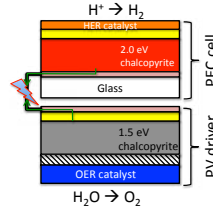


Material cost :100\$/m², STH: 5-10%

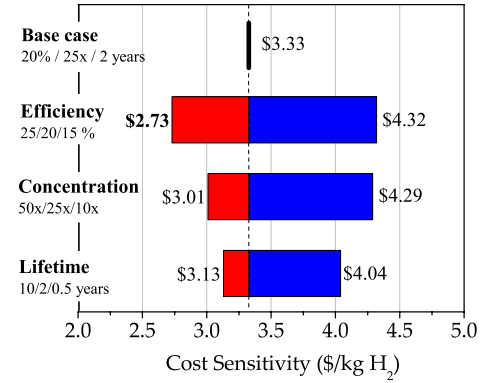


This project's goal (2017)

Stacked hybrid device

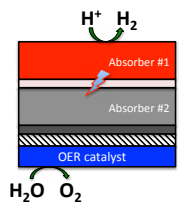


Material cost: 200\$/m², STH target > 15%

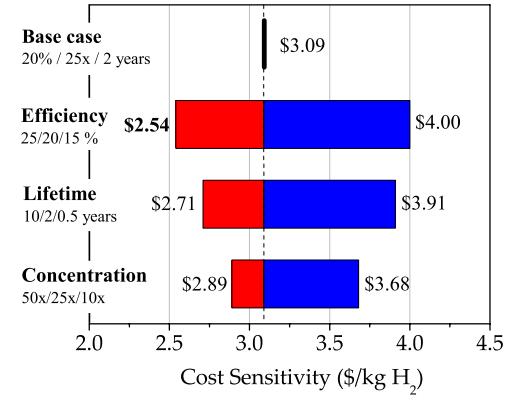


Ultimate goal (>2020)

Monolithic hybrid device



Material cost: 60\$/m², STH target = 25%



- Using current technology (co-planar CIGSe @ 10% STH), current material cost (100 \$/m²) and 6-month durability: **6.6 \$/kg H₂**
- Mechanical stack with 15% STH, 200 \$/m² device cost and 2-year durability: **4.3 \$/kg H₂**
- Monolithic device with 25% STH, 60 \$/m² and 2-year lifetime: **2.5 \$/kg H₂**

Accomplishments - Response to reviews' comments

“It would be useful for the team to show a schematic that illustrates the team’s vision for what the complete, integrated device for real world application might look like. It is not clear how ion transport between the front and the back of the device would be achieved.”

- Our project aims to develop wide bandgap chalcopyrite photocathodes. A mechanical stack approach will be used to pair these electrodes with existing high efficiency PV drivers to form a complete HPE device (proof of concept). However, our techno-economic analysis indicates that this approach is not economical for large scale PEC H₂ production. To be economically viable, a commercial device should be made of two absorbers monolithically integrated on the same substrate, with hydrogen and oxygen evolved on opposite sides of the device. For this reason, our team has chosen to study some key components of the monolithic structure (e.g. IMO as intermediate transparent window layers) to identify possible pitfalls.
- Ion transport between the front and back can be achieved via re-circulation of the electrolyte between the two sides of the device. Other engineering solutions, including JCAP’s louver designs, can be used to overcome ion transport issues.

“For the development of new buffers, it would be great to see more direct measurements of band alignment”

- This is indeed an important aspect of our project. It should be noted that the complete band alignment of one absorber/buffer system is not trivial and could take 6 months to a year. For this reason, our buffer selection is primarily guided by theoretical modeling. A first set of CdS-coated wide bandgap chalcopyrite samples were sent to UNLV. Preliminary measurements were performed on CdS, CIGS₂ and CdS/CIGS₂ samples to validate sample preparation and handling (“zero sample set”). Only a few series of absorbers/buffers will be considered for complete band alignment analysis.

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,

Project-specific collaborations:

- [Stanford, UNLV, LLNL and NREL](#): partners in this project (**ALL TASKS**),
- [University of Louisville \(M. Sunkara\)](#): photoluminescence on CuGaSe_2 materials (**TASK 1**),
- [Jozef Stefan Institute-Slovenia \(M. Mozetic\)](#): U.S./European project on sulfides (CIGS2) (**TASK 1**),
- [EMPA \(A. Braun\)](#): in-situ characterization of phase transformation during CIGS synthesis (**TASK 1**),
- [University of Los Andes-Colombia \(S. Barney\)](#): reactive sputtering of ZnOS buffers (**TASK 2**),
- [University of Bordeaux-France \(A. Rougier\)](#): development of temperature-resistant TCOs as intermediate layers for multi-junction CIGS 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)S₂ absorbers

Challenges/Barriers: sub-bandgap transmission of sulfides (CIGS₂, CGSSe: T=40-50%) lower than that of selenides (CIGSe, CGSe: T=80%).

Proposed Future Work:

- identify impurities in sulfide compounds (UNLV), assess their impact on opto-electronic properties (LLNL) and evaluate mitigation strategies (HNEI, Stanford and NREL).
- study new wide bandgap selenide absorbers, e.g. CuInAlSe and CuInBSe, and evaluate transmission/photoactivity

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

Challenges/Barriers: free electron losses (E_g-V_{oc}) appear to be greater with sulfides than selenides.

Proposed Future Work:

- continue testing of alternative buffer layers, including ZnOS and CdZnS.
- CIGS/buffer interface will be characterized at UNLV.

Task 3. Surface catalysis and corrosion resistance

Challenges/Barriers: new MoS₂ and TiO₂ ALD coating successfully developed, yet CIGSSe durability limited to 250 hours

Proposed Future Work:

- identify origin of degradation at microscopic level (pin holes, grain boundaries)
- continue development of ALD coatings, including MoS₂, TiO₂ and SiO₂,
- identify optimum protective material for durability.

Task 4. Device certification and efficiency benchmarking

Challenges/Barriers: achieving high STH efficiency with mechanically stacked devices will be challenging (optical & electrical losses).

Proposed Future Work:

- continue development of temperature resistant TCO,
- integrate wide bandgap chalcopyrites on robust PV driver (starting with c-Si),
- assess electrical behavior of CIGSe/CdS junction (future bottom cell) as function of temperature

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 materials for both HER catalysis and corrosion protection and assess the STH efficiency of the complete HPE device.

Accomplishments

(1) Developed two new wide bandgap chalcopyrite material systems (CGSSe and CuGa_3Se_5) with optimum optical properties for PEC H_2 production, (2) successfully fabricated CIGS_2 , CGSSe and CuGa_3Se_5 absorbers with $E_g > 1.7\text{eV}$ generating over 10 mA/cm^2 (in both PV & PEC integration), (3) reached 730 mV Voc with CdS and developed alternative buffer materials for wide E_g chalcopyrites (ZnOS), (4) succeeded in measuring S $L_{2,3}$ in-situ at the solid/liquid interface and (5) developed new ALD protective coatings (MoS_2 and TiO_2) to improve durability.

Collaborations

Project-specific collaboration with U.S. and international teams to address barriers in each of the 4 technical tasks.

Proposed future work

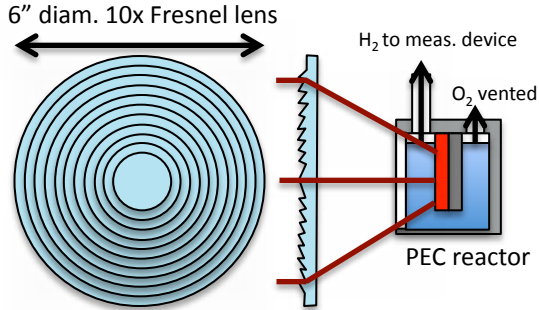
(1) Continue development of PV-grade chalcopyrites and demonstrate at least 12 mA/cm^2 with 1.7eV absorbers, (2) fabricate, characterize and test ZnOS as an alternative buffer to CdS and demonstrate Voc > 750 mV (FY16 Go/NoGo), (3) continue development of conformal MoS_2 and TiO_2 coatings using ALD to meet 750 (FY16) and 1,000 (FY17) hour durability targets and (4) compare monolithic vs. mechanically stacked HPE devices in both PV and PEC configuration.

Technical back-up slides

Complete PEC device fabrication

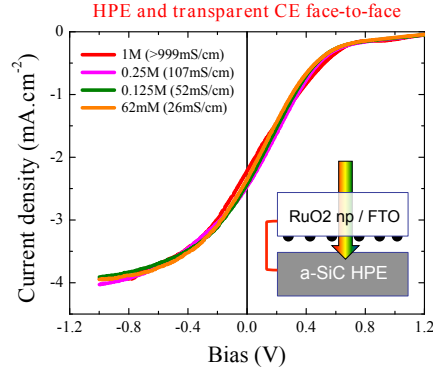
1. PEC reactor designs

Option 1: PEC and CE back-to-back



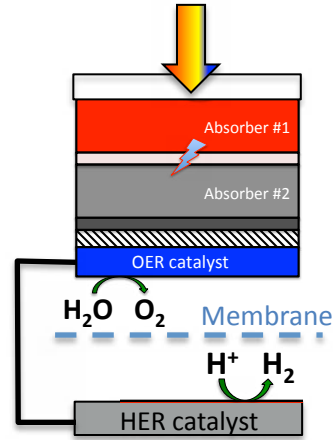
→ Electrolyte circulation needed

Option 2: PEC and CE face-to-face



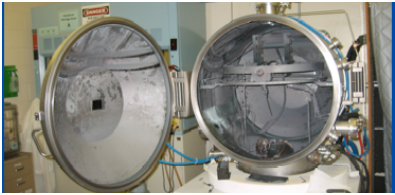
→ Gas separation needed

Option 3: superstrate PEC system



2. Fabrication of large PEC devices

HNEI's capabilities

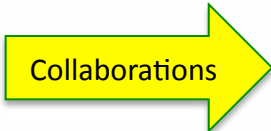


CIGSe evaporation chamber

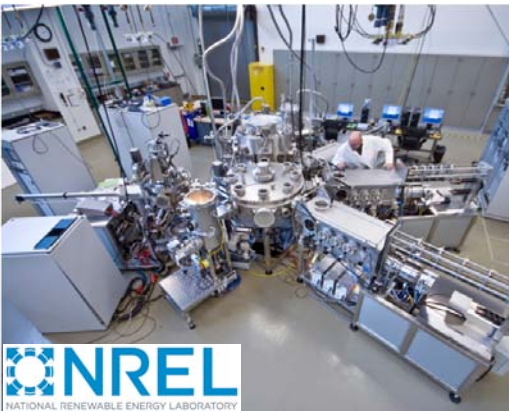


Sulfurization capsule

Sample size: 1"x1"

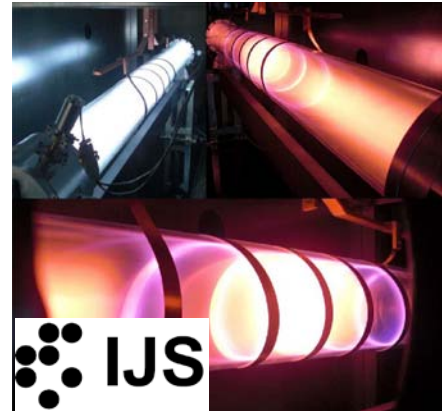


NREL's CIGSe large cluster tool



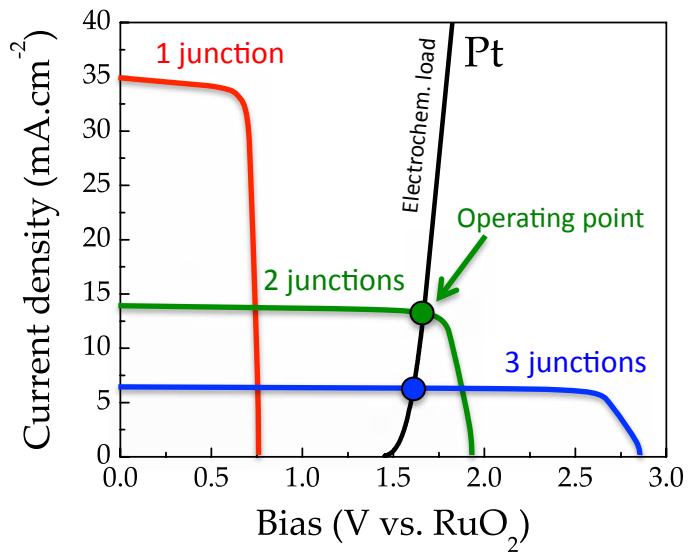
Sample size: 6"x6"

Josef Stefan Institute's H2S reactors



Sample size: 1 m²

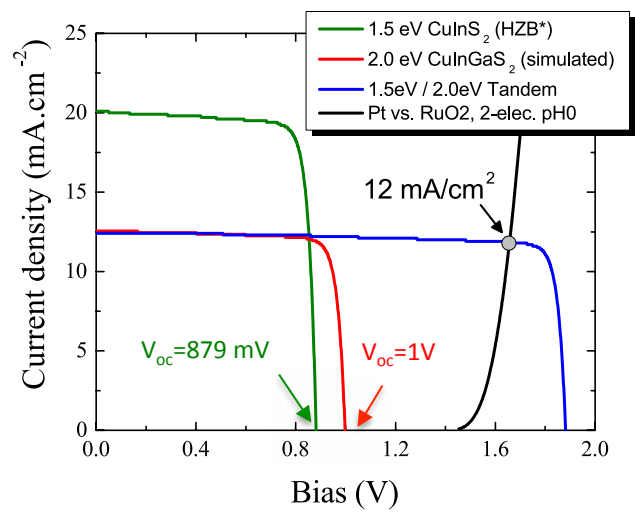
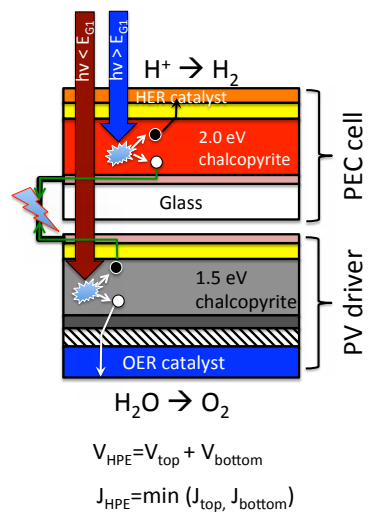
Device requirements for high efficiency H₂ PEC production



PEC device ↔ solid-state solar cell in series with an electrochem. load

- 1 junction: bias too low for water splitting, $\eta_{STH} = 0\%$
- 2 junctions: optimum current and bias, $12\% < \eta_{STH} < 25\%$
- 3 junctions: high bias but low current, $\eta_{STH} < 10\%$

Simulations of the complete PEC system to identify solid-state requirements:

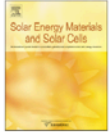
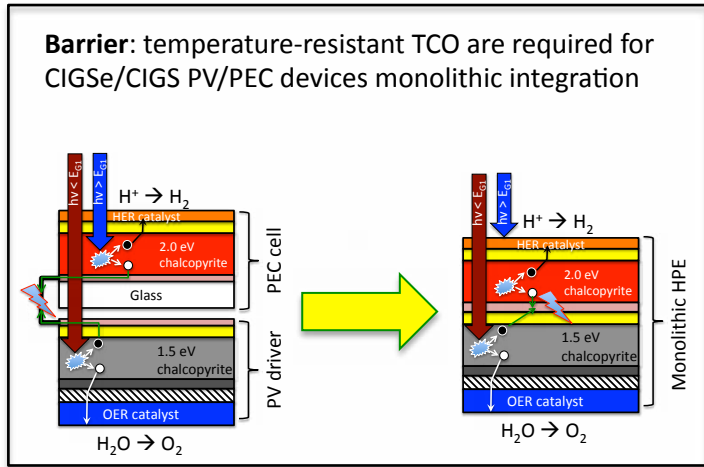


1. Requirement for 15% STH:

- Bottom cell: 1.5eV, $V_{oc} = 879$ mV
- Similar to Helmholtz Center Berlin's CIS₂ cell
- Top cell: 2.0eV, $V_{oc} \approx 1.0$ V, $J_{sc} \approx 12-13$ mA.cm⁻²
- This project goal

2. Requirement for 25% STH:

- Bottom cell: 1.1eV, $V_{oc} = 740$ mV
- Similar to ZSW's CIGSe₂ cell
- Top cell: 1.74eV, $V_{oc} \approx 1.0$ V, $J_{sc} \approx 20-22$ mA.cm⁻²
- Ultimate goal

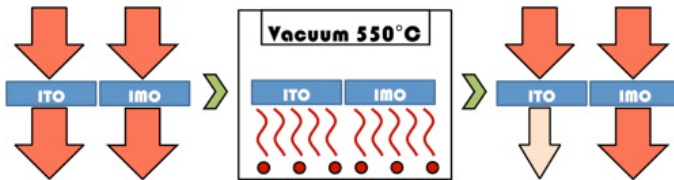


Temperature-resistant high-infrared transmittance indium molybdenum oxide thin films as an intermediate window layer for multi-junction photovoltaics

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^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 ($\Omega\text{-cm}$) $\pm 0.02 \times 10^{-4}$
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

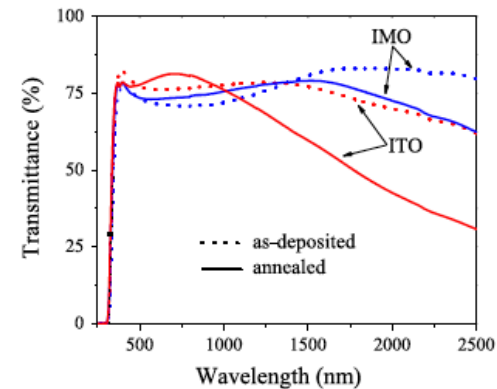


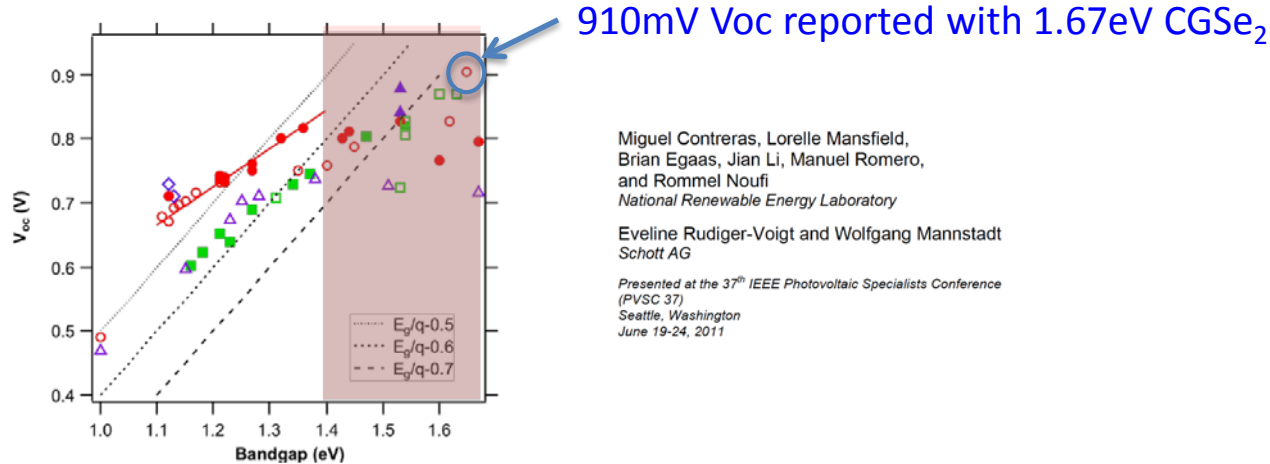
Fig. 1. Optical transmittance of typical IMO and ITO samples measured from 250 to 2500 nm. Infrared transmittance of IMO remains high even after annealing whereas that of ITO has decreased significantly.

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

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

Reported PV-grade “intermediate bandgap” CIGSe and “wide bandgap” CIGS

a. CIGSe (NREL)



b. CIGS (HZB)

