PD053

PHOTOELECTROCHEMICAL HYDROGEN PRODUCTION

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MVSystems, Inc.
May 12, 2011

Project ID # DE-FC36-07GO17105, A00

Overview

Timeline

Phase 1:
- Project start date: 9/1/2007
- Project end date: 12/31/2010

Passed go/no go evaluation in Nov, 2010

Phase 2:
- Project start date: 1/1/2011
- Project end date: 12/31/2012

Budget

- Total project funding
  - DOE share: $2,970,172
  - Contractor share: $820,000

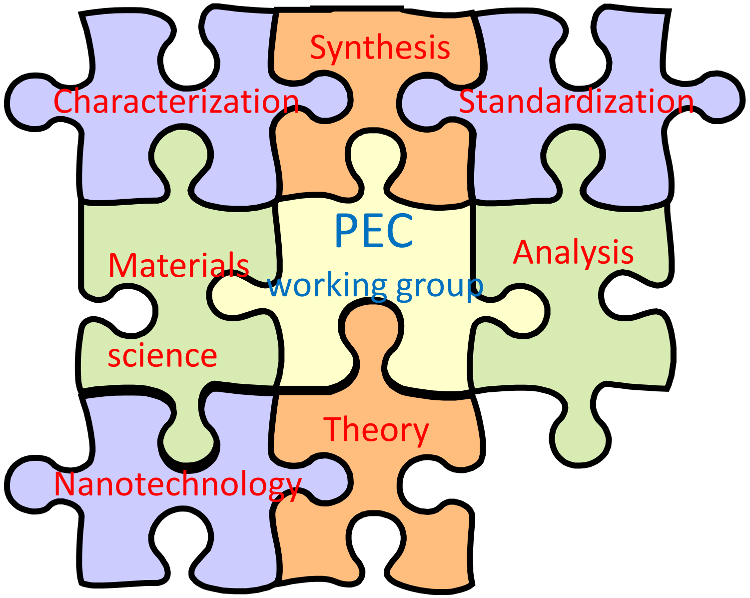
Barriers

- 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.

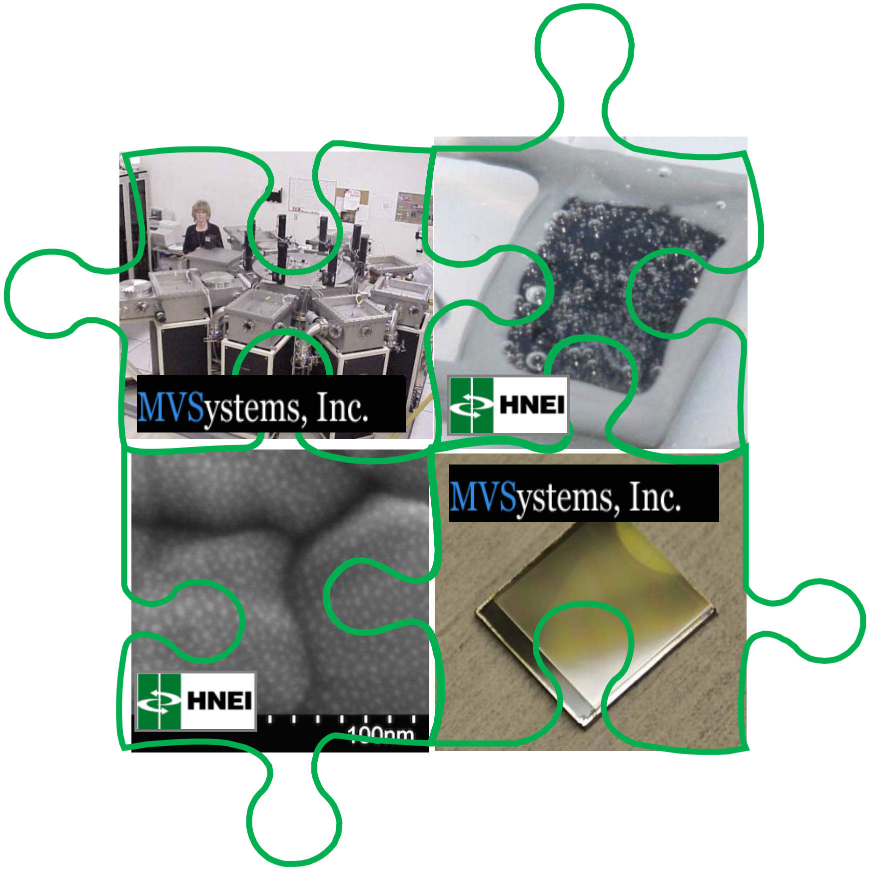


PEC Working Group:
Evaluating working directions
Sharing and building-up knowledge
Accelerating research progress

➢ Thin-Film Materials for Cost-Effective 2nd Generation PEC Devices

- a-SiC
- WO_3
- CGSe

} powered by a-Si tandem solar cell

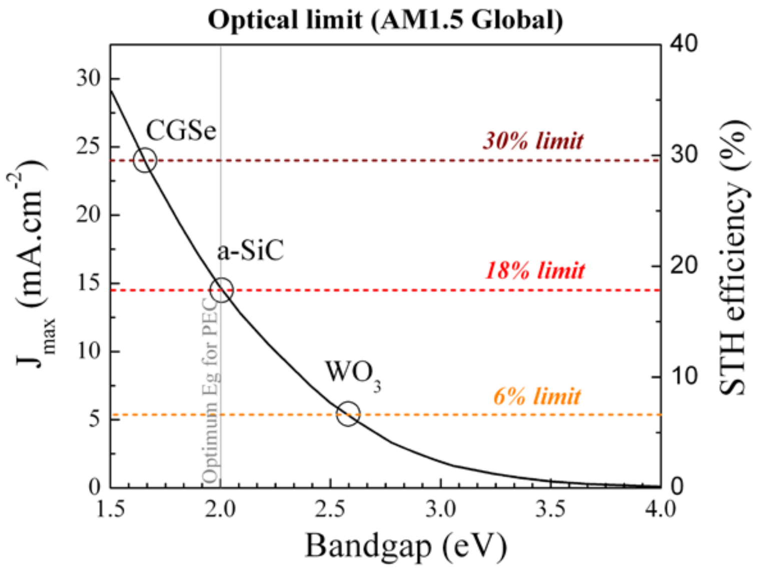


DOE Targets: >1000h @STH > 8% (2013)
\$2 - 4/kg H_2 projected PEC cost
(beating >\$10/kg H_2 for PV-electrolysis)

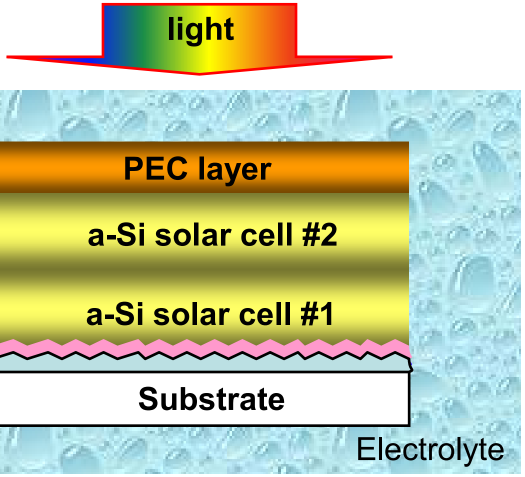
Relevance - Objectives

3 material classes covered in this project:

- Amorphous silicon carbide (a-SiC)
  - *(performed by MVS)*
- Tungsten oxide (WO3)
  - *(performed by HNEI)*
- I-III-VI$_2$ (Copper Chalcopyrite-based)
  - *(performed by HNEI)*



Our goal: Develop a monolithic hybrid PEC device powered by MVS' low-cost a-Si-based tandem solar cell.



Project Objectives:

- Solar-to-hydrogen efficiency: 5%
- Durability: 1) 200-hrs (current milestone)
  2) 500-hrs (by the end of Phase II)

Relevance -Milestones

Goal ->	Material Photocurrent 4mA/cm^2	Material/Device Durability* 200hrs	Device Efficiency (STH) 5%
Amorphous Silicon Carbide (a-SiC)	8mA/cm2 *>100% Achieved*	310hrs *>100% Achieved*	1.6%STH *32% Achieved*
Tungsten Oxide (WO_3)	3.6mA/cm^2 *90% Achieved*	250hrs *>100% Achieved*	3.1%STH *60% Achieved*
I-III-VI_2 (Copper Chalcopyrite-based)	20mA/cm^2 *>>100% Achieved*	200hrs *100% Achieved*	4.3%STH *85% Achieved*

*** Test conditions in slide #24.**

Relevance – Barriers

	a-SiC	WO_3	I-III-VI_2 (Copper Chalcopyrite-based)
AB: Synthesis	Entire PEC device fabricated with low-cost PECVD in an cluster tool identical to those used in PV industries.	Best performance achieved with conventional sputtering methods	CGSe films synthesized with co-evaporation methods. Synergy with PV industry (CIGSe)
AC: Device design - Achieved: **- Barriers:**	Monolithic device **No**	Hybrid PEC device concept demonstrated with mechanical stack **Current deposition temperature requires innovative integration scheme**	Hybrid PEC device concept demonstrated with co-planar PV/PEC **Current deposition temperature requires innovative integration scheme**
Z: Durability - Achieved: (so far tested) **- Barriers:**	310-hrs **No**	250-hrs **No**	200-hrs **No**
Y: Efficiency - Achieved: **- Barriers:**	Limited STH (1.6%) compared to the solid state version (>5%) **Need to modify surface to lower overpotential**	3.1% STH with pure WO_3 (2.6 eV). **Need to reduce material bandgap to increase light absorption**	4.3% STH achieved with co-planar integration. **Need to modify band alignment to lower onset potentials**

Approaches

Synergetic work on 3 different material classes

1) All 3 hybrid PEC devices will use the same a-Si tandem solar cell “engine”

--> each improvement on the solar cell design benefits to the entire program

2) Both photo-anodes and photo-cathodes are evaluated under one program

--> Discovery on new surface catalysts can be implemented to new counter electrodes

3) All 3 material classes performances are evaluated in the same laboratory

--> all tests are performed under identical experimental conditions facilitating comparison

3 major tasks to improve STH efficiency

a-SiC: improve interface energetics and kinetics with appropriate surface treatment
- *decrease overpotential*

WO_3: identify stable alloys with appropriate band gap
- *decrease bandgap from 2.6~2.8 eV to close to 2.0 eV*

I-III-VI_2: lower valence band edge via Cu and Se (partial) substitution
- *decrease overpotentials and increase bandgap from 1.6 to 1.9 eV*

Part I

Amorphous Silicon Carbide (a-SiC)

Presenter: *Jian Hu*, MVSystems, Inc

Part II

Tungsten Oxide (WO3) Compounds

Presenter: *Nicolas Gaillard*, Hawaii Natural Energy Institute

Part III

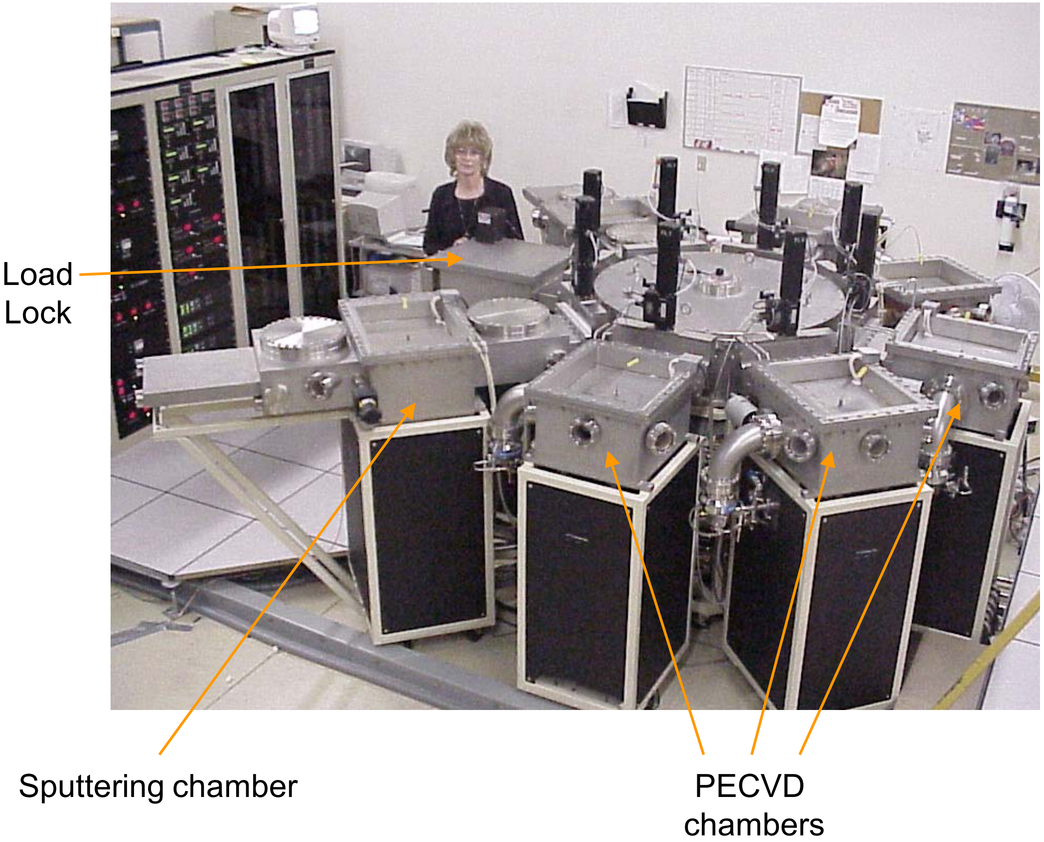
Copper Chalcopyrites (CIGS)

Presenter: *Nicolas Gaillard*, Hawaii Natural Energy Institute

a-SiC: Cluster Tool PECVD/Sputtering System

Addressing “AB”

All a-SiC films, photoelectrodes, solar cells and the PEC hybrid devices were fabricated in the cluster tool PECVD/Sputtering System, designed and manufactured by MVSystems, Inc.



Main deposition parameters:

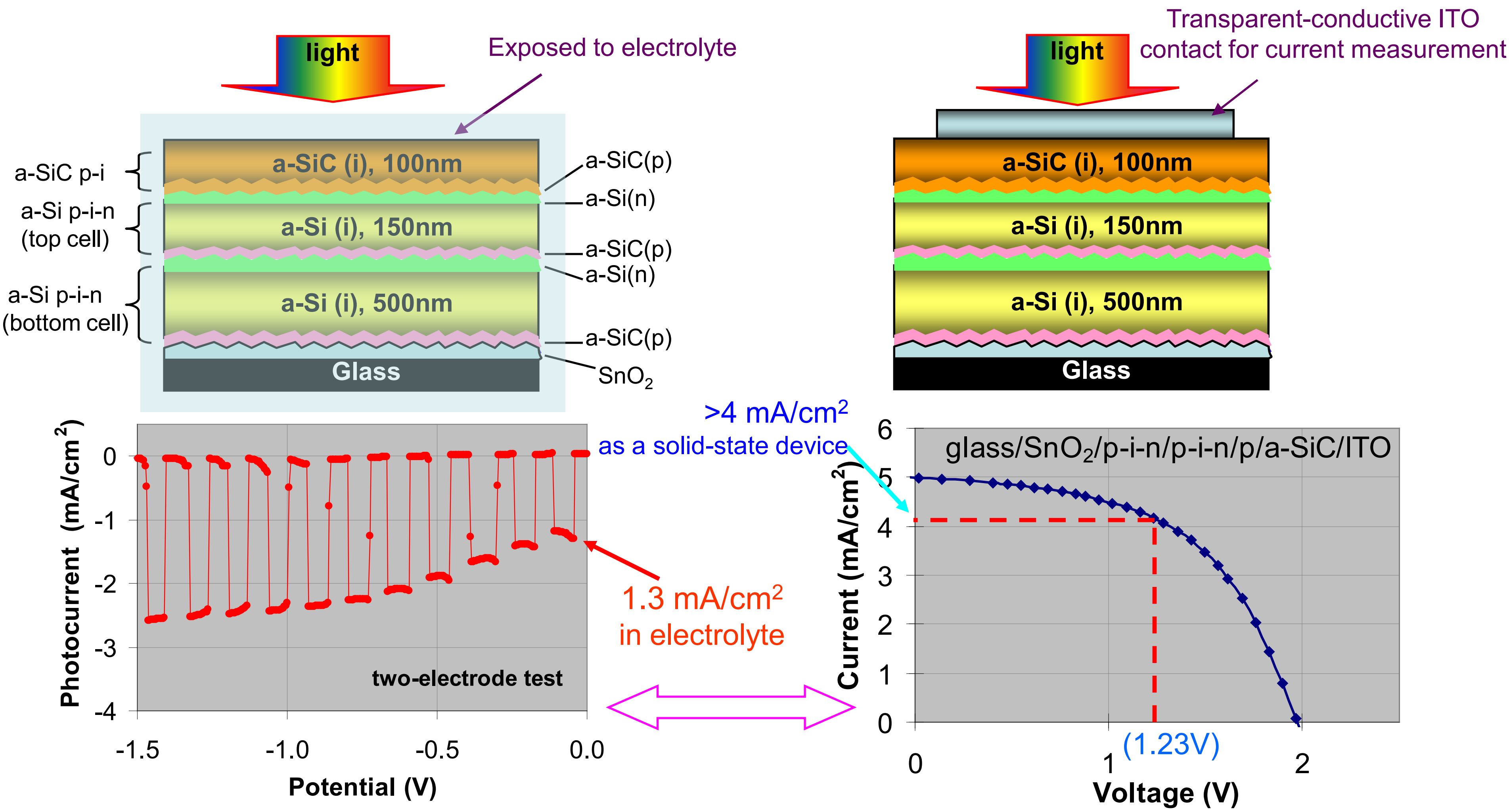
RF power:	**10-20 W**
Excitation frequency:	**13.56 MHz**
Pressure:	**300-550 mTorr**
SiH_4 flow rate:	**20 sccm**
CH_4 flow rate:	**0-20 sccm**
H_2 flow rate:	**0-100 sccm**
Substrate temperature:	**200° C**

http://www.mvsystemsinc.com

Amorphous and/or nano-crystalline Si solar cells in conjunction with the photo-electrode as the driver for a-SiC, WO3 and I-III-VI_2 PEC.

Progress: Comparison with a Solid-State Configuration

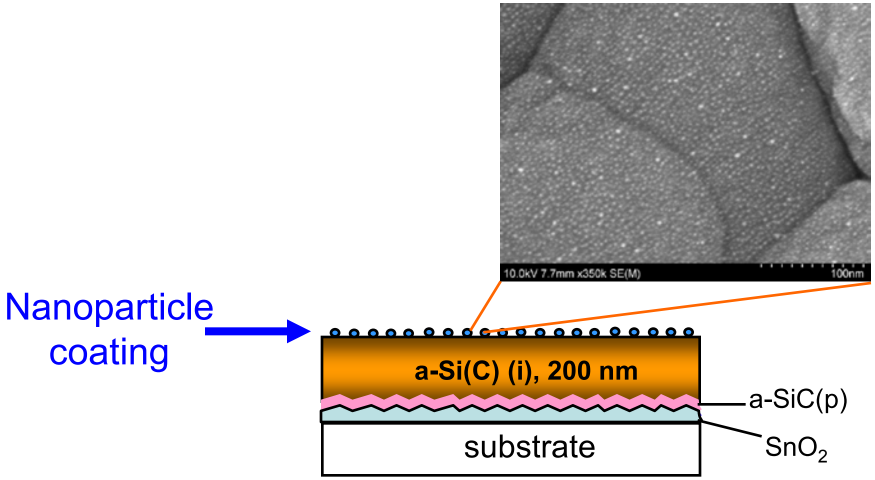
Addressing “Y”

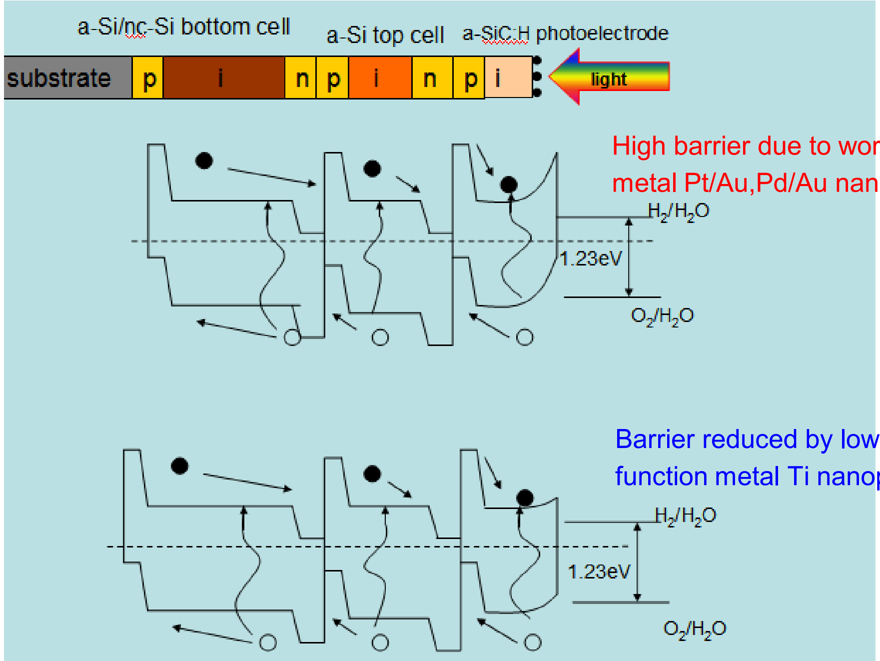


- ➢STH efficiency of hybrid PEC cell should be >6% base on solid state version (right)
- ➢Low current in hybrid PEC cell (left)
- ➢<u>Charge carrier extraction problem at the a-SiC/electrolyte interface</u>

Progress: Surface Modification – Use of Metal Nanoparticles

Addressing "Y"



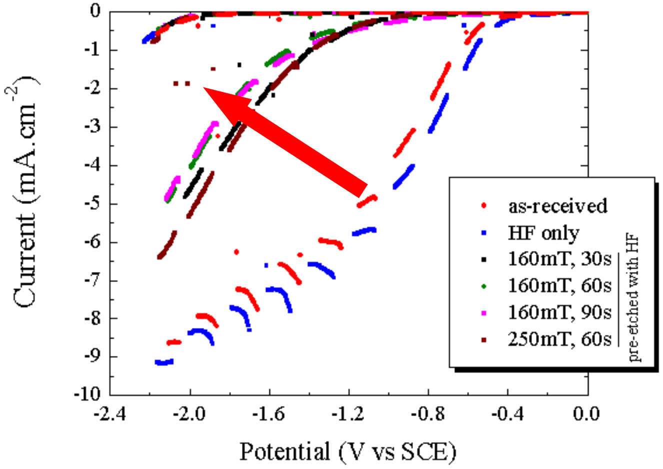


High barrier due to work function metal Pt/Au,Pd/Au nanoparticle

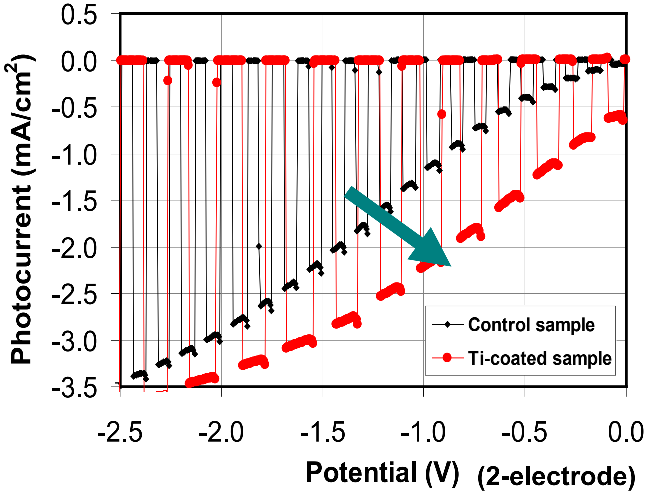
Barrier reduced by low work function metal Ti nanoparticle

The band diagram at a-SiC/electrolyte interface with high and low work function metal nanoparticle

- **High work function material (Pt, Pd, Au): decrease photocurrent (due to Schottky barrier)**



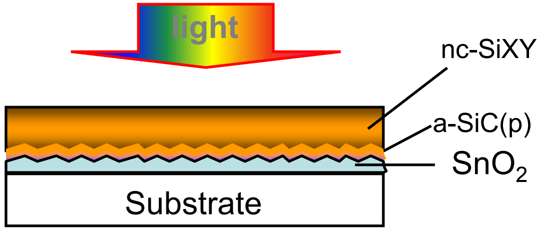
- **Low work function material (Ti): increase photocurrent**



Progress: improvement of **a-SiC** interface energetics and kinetics

- Develop nanocrystalline Si based thin film for surface modification

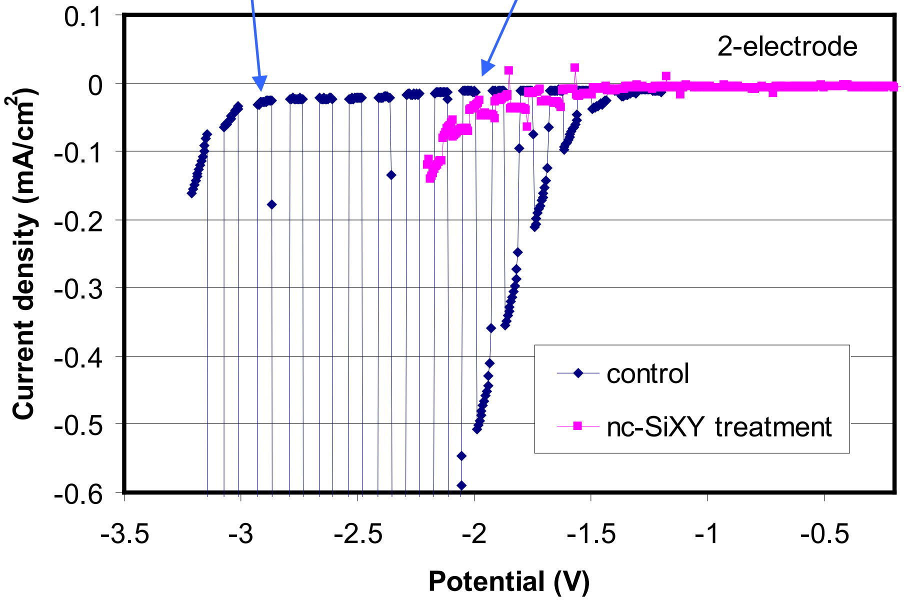
Addressing "Y"



nc-SiXY photoelectrode

Dark current onset of a-SiC electrode

Dark current onset of nc-SiXY electrode



Distinctive features of nano-crystalline SiXY:

- A much higher dark conductivity, i.e., 10^{-9}-10^{-8} S/cm vs. $<10^{-12}$ S/cm (a-SiC).
- Low dark current onset potential, i.e., -1.5 V vs. -3 V (a-SiC electrode).

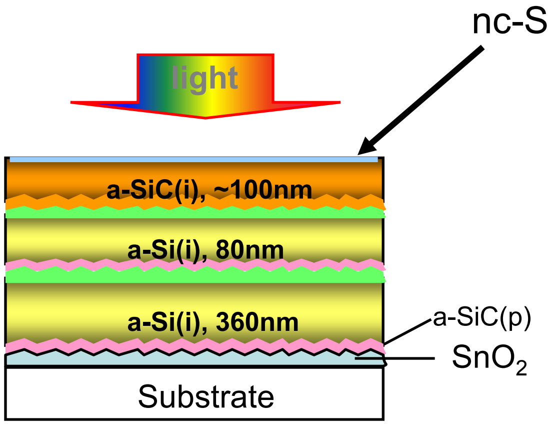
nc-SiXY could be used as a transparent catalyst for HER.

[Data measured by HNEI]

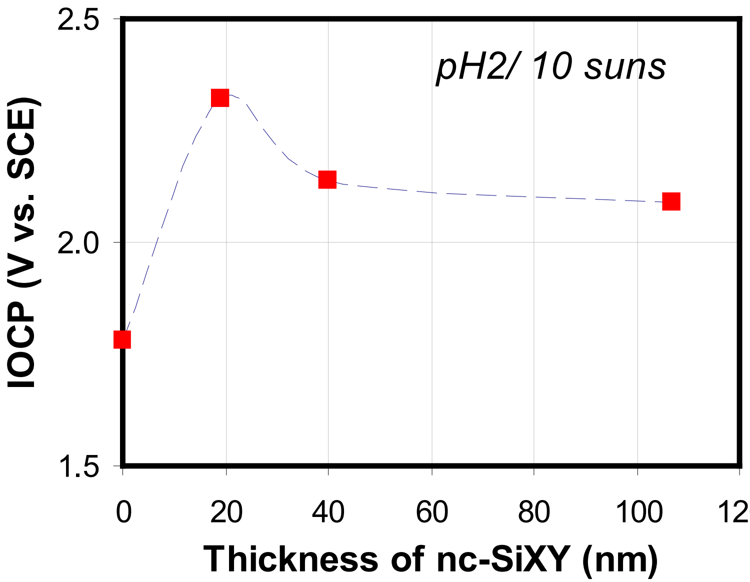
Progress: improvement of **a-SiC** interface energetics and kinetics

- Applying nc-SiXY for surface modification

Addressing “Y”

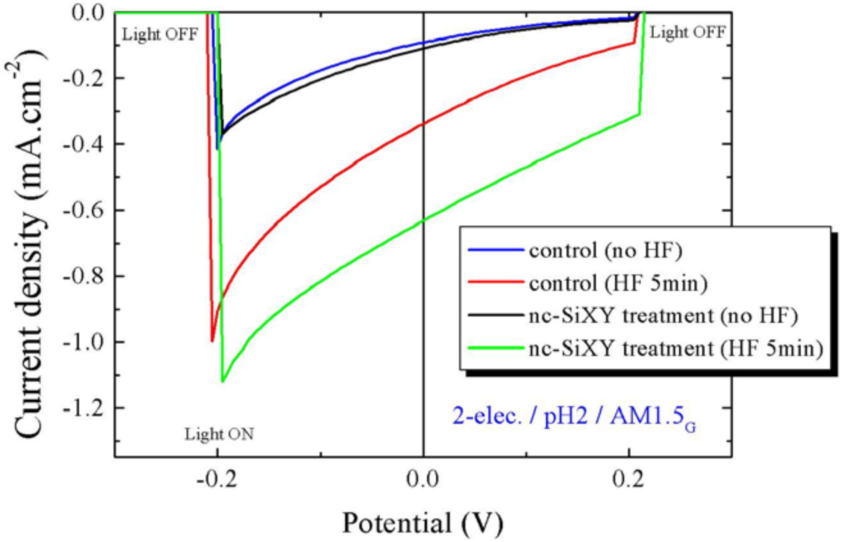


PV/a-SiC hybrid device



<u>Measurement of V_{FB}</u>: Illuminated open circuit potential (IOCP); high illumination (approx. 10 suns).

- **Strong impact of nc-SiXY on V_{fb} (anodic shift): improvement of PEC perf**
- **Best improvement with thin nc-SiXY layer (19nm)**
- **Higher photocurrent at zero bias**.



[Data measured by HNEI]

Future Work (a-SiC PEC electrode)

- ❑ Improvement of photocurrent in the hybrid PEC cell.

Focus˜ minimize over-potential losses to enhance the photocurrent

1. Modify the surface structure of intrinsic a-SiC using the following approaches,
   a. nano-crystalline SiXY (MVS proprietary material already developed);
   b. CH_3 termination.

2. Analyze the surface structure of the a-SiC photoelectrode. *(This work will be in collaboration with UNLV and NREL group)*

3. Development of new type of electrolyte. *(This work will be in collaboration with NREL group)*

- ❑ Durability tests.
  - Extend the durability period to >500 hours.

- ❑ Additional materials evaluation: nc-SiXY, a-SiCN, nc-SiNx, a-SiON

Part I

Amorphous Silicon Carbide (a-SiC)

Presenter: *Jian Hu*, MVSystems, Inc

Part II

Tungsten Oxide (WO3) Compounds

Presenter: *Nicolas Gaillard*, Hawaii Natural Energy Institute

Part III

Copper Chalcopyrites (CIGS)

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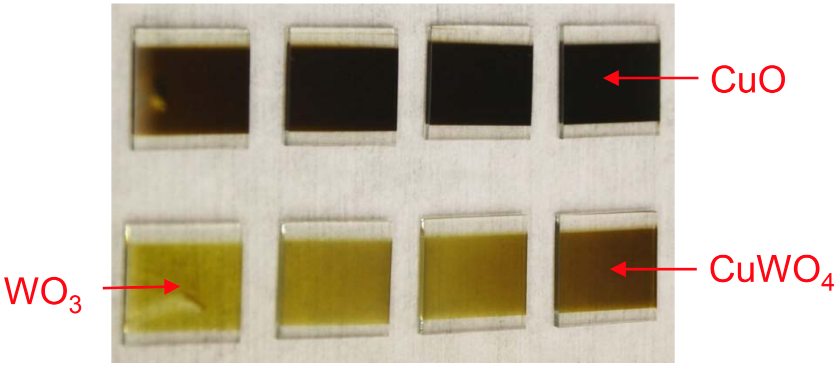
Progress: reduction of WO_3-based material bandgap

Addressing "Y"

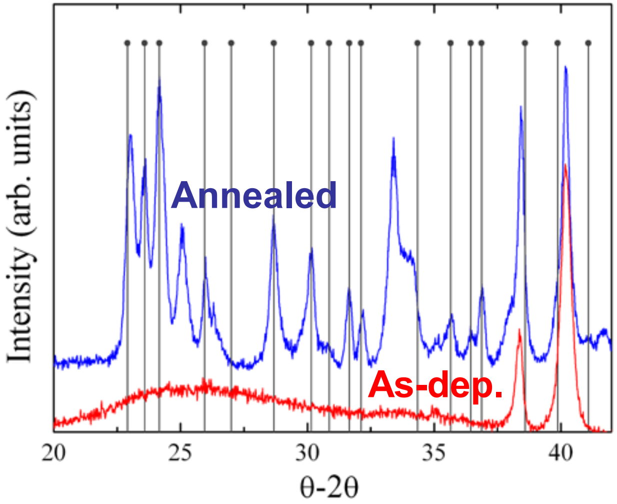
One must identify thermodynamically stable W-based alloys with Eg close to 2.0 eV

Approach #1: $CuWO_4$ "combinatorial" survey using co-sputtering process

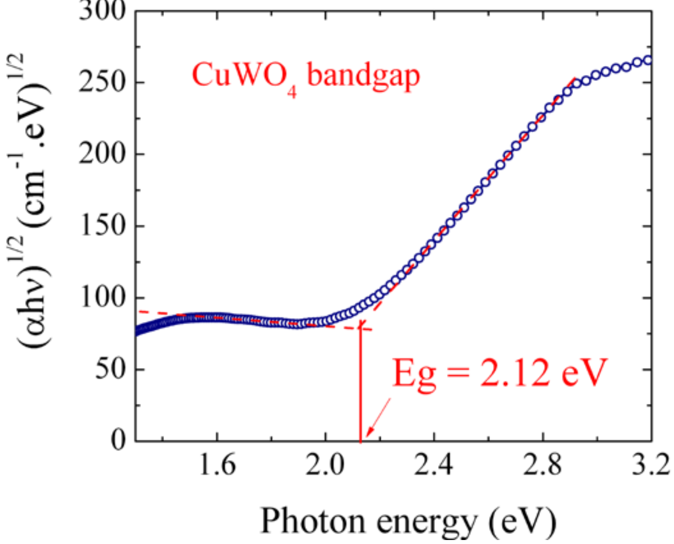
$(CuO)_x(WO_3)_{1-x}$ films obtained by co-sputtering



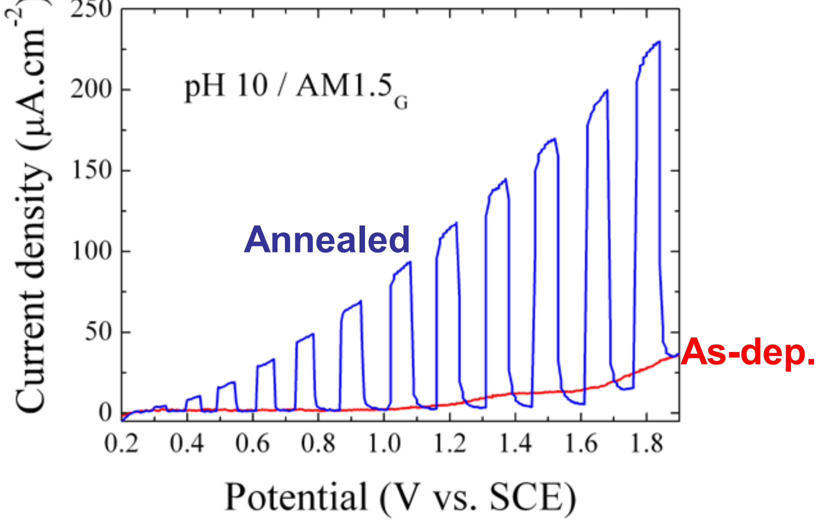
Crystalline $CuWO_4$ after 450°C annealing



$CuWO_4$ thin films with near ideal E_G



PEC measurement



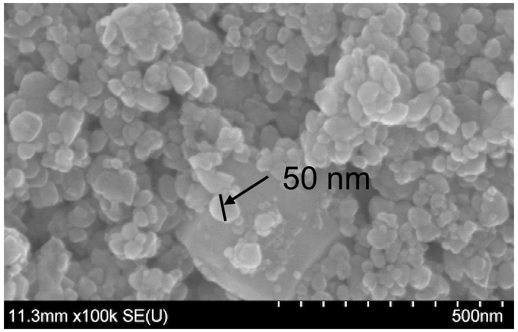
Progress: reduction of WO_3-based material bandgap

Addressing “Y”

Approach #2: $CuWO_4$ thin film synthesis from nano-particles or liquid precursors

Main advantages over conventional co-sputtering process:

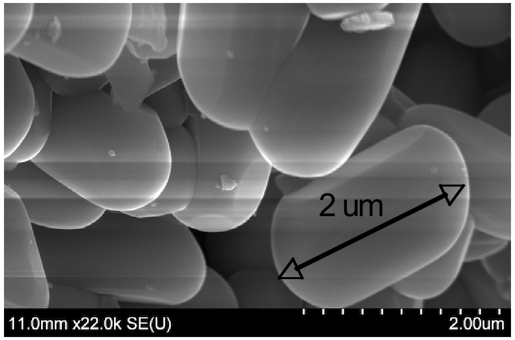
1. Uniform deposition: no material gradient over the substrate
2. Ease of material tailoring: doping can be done by adding appropriate element to the blend



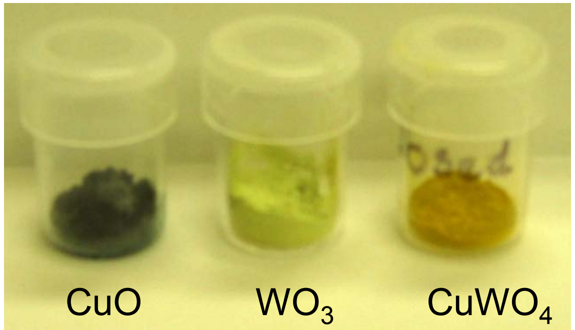
From CuO & WO_3 nanopowders…

sintering

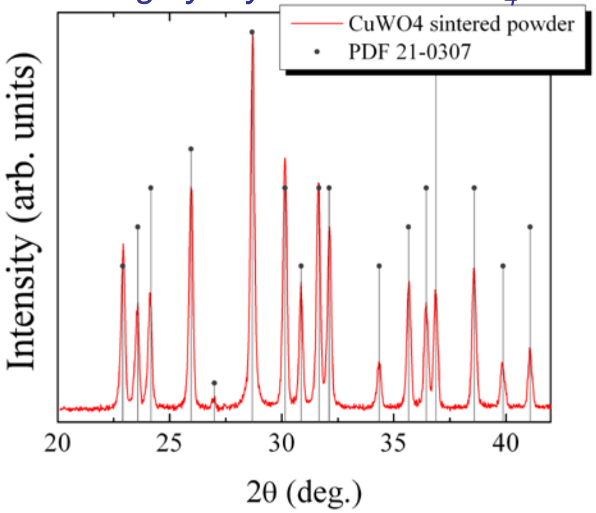
… to $CuWO_4$ micro-grains



(800°C for 5 hrs)



Highly crystalline $CuWO_4$



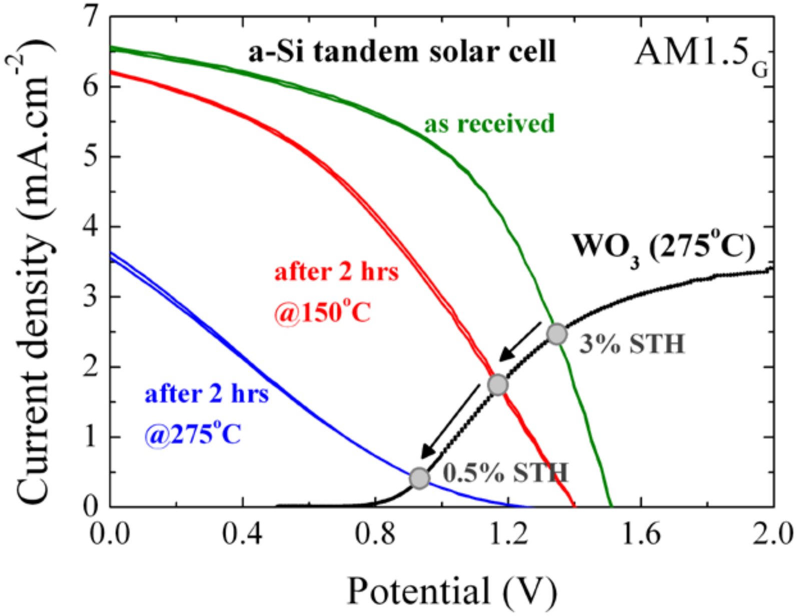
Progress: new monolithic integration for Hybrid PEC device

Addressing "AC"

Main barrier: a-Si solar cells performances degraded after long exposure to heat

Issue

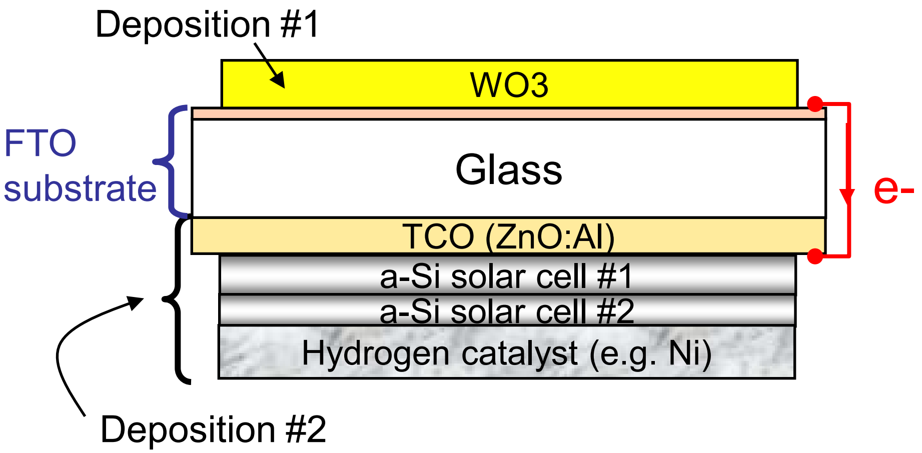
Effect of heat exposure on (WO_3 filtered)
a-Si tandem solar cell performances



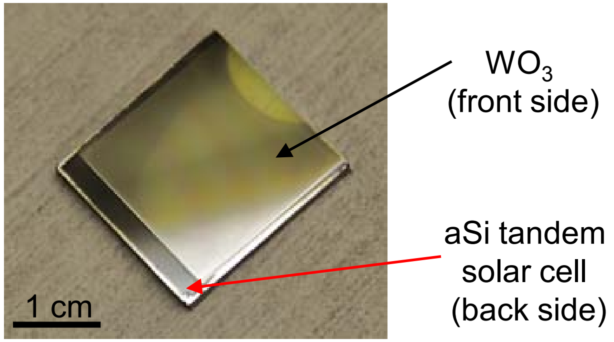
The conventional hybrid PEC electrode approach (with PEC layer deposited on top of solar cells) is not compatible for WO_3 and low-cost a-Si tandem solar cells.

Solution

Deposition #1: WO_3 on front side
Deposition #2: inverted a-Si on back side



Picture of PEC hydrid device



Future Work (WO_3 PEC electrode)

Improve the electrical conductivity of $CuWO_4$ thin films

→ Identify appropriate doping elements (collaboration with NREL)
→ Validate selected dopants using powder sintering and electrodeposition methods

Pursue durability test up to 500-hrs

→ Understand possible degradation mechanisms (if any)
→ Evaluate surface passivation methods (in situ measurement at UNLV)

Test fully integrated WO_3-based PEC hybrid device

→ Validate the front / back side integration scheme
→ Perform extensive indoor and outdoor test with H_2 production quantification.

Part I

Amorphous Silicon Carbide (a-SiC)

Presenter: *Jian Hu*, MVSystems, Inc

Part II

Tungsten Oxide (WO3) Compounds

Presenter: *Nicolas Gaillard*, Hawaii Natural Energy Institute

Part III

Copper Chalcopyrites (CIGS)

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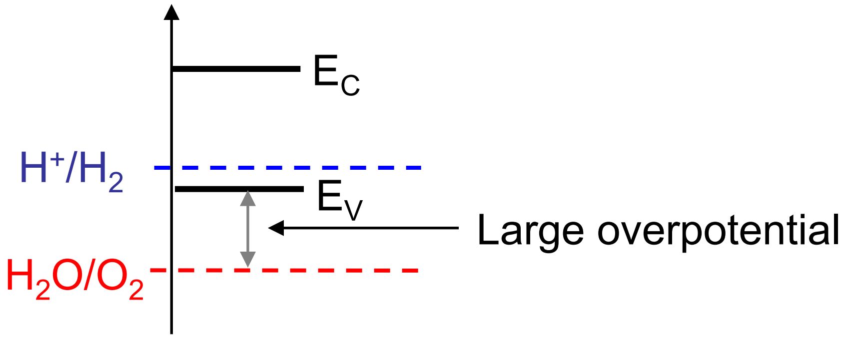
Progress: bulk modifications of CGSe baseline

Addressing "Y"



Barriers:

- Bandgap (1.65 eV) currently too small
- Overpotential too high

Approach #1: Addressing both barriers by lowering valence band-edge with elemental substitution of Ag and/or Sulfur

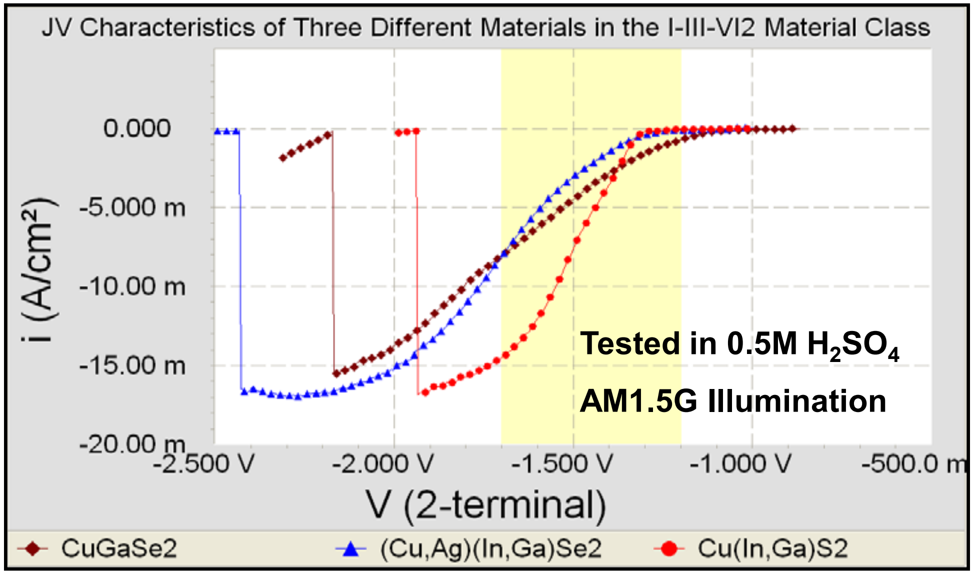
Bandgap:

$CuGaSe_2$ = 1.65eV (baseline)

$(Cu,Ag)(In,Ga)Se_2$ up to 1.85eV

$Cu(In,Ga)(Se,S)_2$ up to 2.43eV

$(Cu_zAg_{(1-z)})(In_xGa_{(1-x)})(S_ySe_{(1-y)})_2$ alloys are bandgap-tuneable

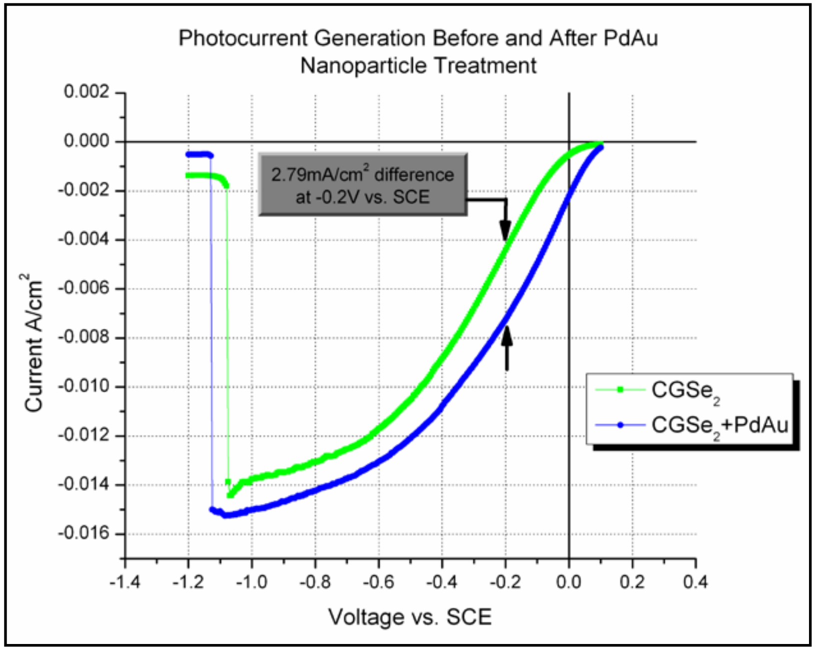


Highlighted in yellow is the voltage region where completed devices typically operate.

Progress: overpotential reduction at CGSe surface

Addressing "Y"

Approach #2: addressing overpotential barrier with catalytic treatment (NREL)

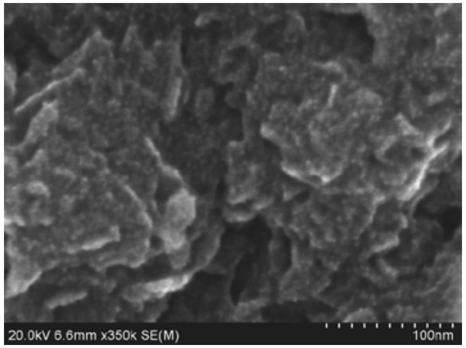


2.79mA/cm² difference at -0.2V vs. SCE

$CGSe_2$ JV characteristics before and after PdAu nanoparticle deposition showing improvement in "fill factor".

PdAu nanoparticles (sputtered)

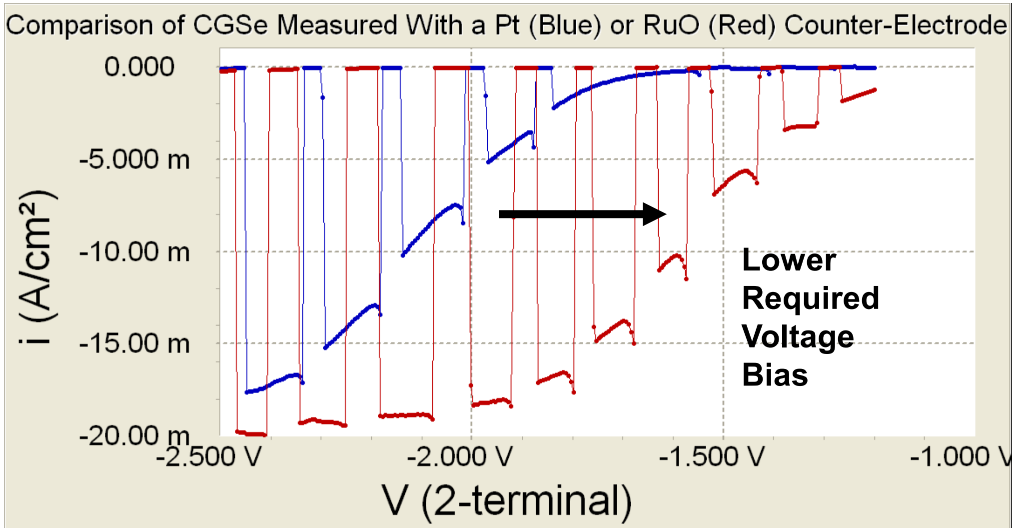
- Onset voltage and saturated photocurrent unchanged, but "fill factor" improved.
- Can essentially squeeze a few more milliamps out of any film



Presence of nanoparticles observed by SEM

Effect of Counterelectrode

- RuO_2 is a far superior oxygen-evolution catalyst when used as an anode with I-III-VI_2 photocathodes



Lower Required Voltage Bias

Progress: STH efficiency with co-planar integration

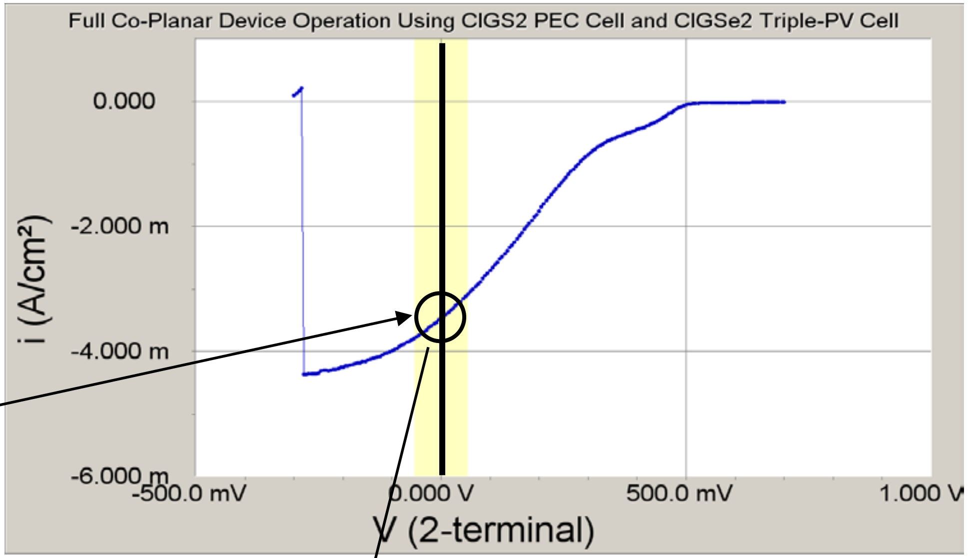
Addressing "AC"

Barrier: Low band gap (1.65eV) materials currently produced require innovative device design

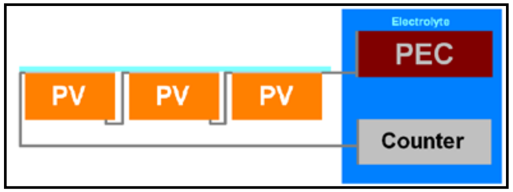
Solution: Large photocurrent produced by materials in this class allow co-planar PV-PEC integration

4.3% STH achieved!

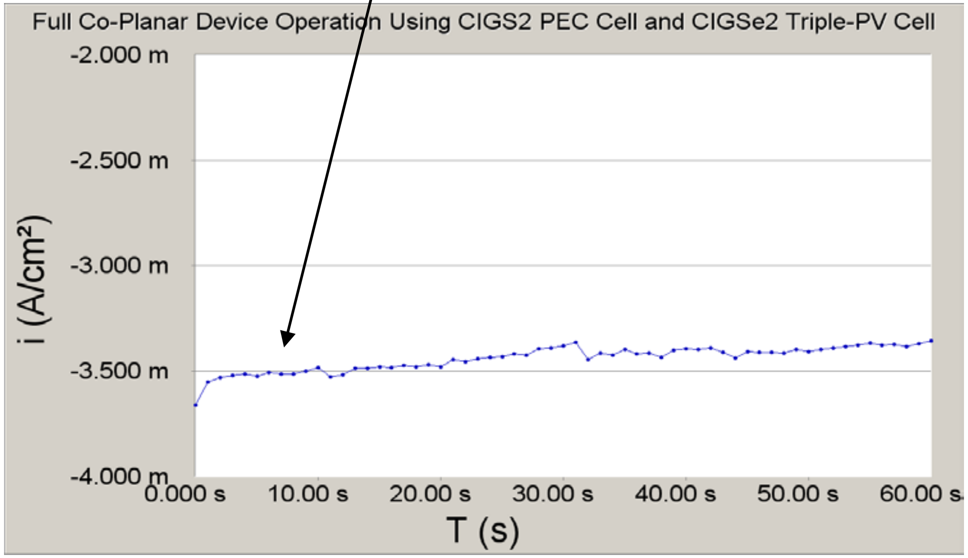
- 3 $CIGSe_2$ PV cells
- $CIGS_2$ (pure sulfide) PEC
- In a standalone device (no external bias):
  - 3.46mA/cm^2 = 4.3%STH



Full Co-Planar Device Operation Using CIGS2 PEC Cell and CIGSe2 Triple-PV Cell



3 PV + PEC serial device



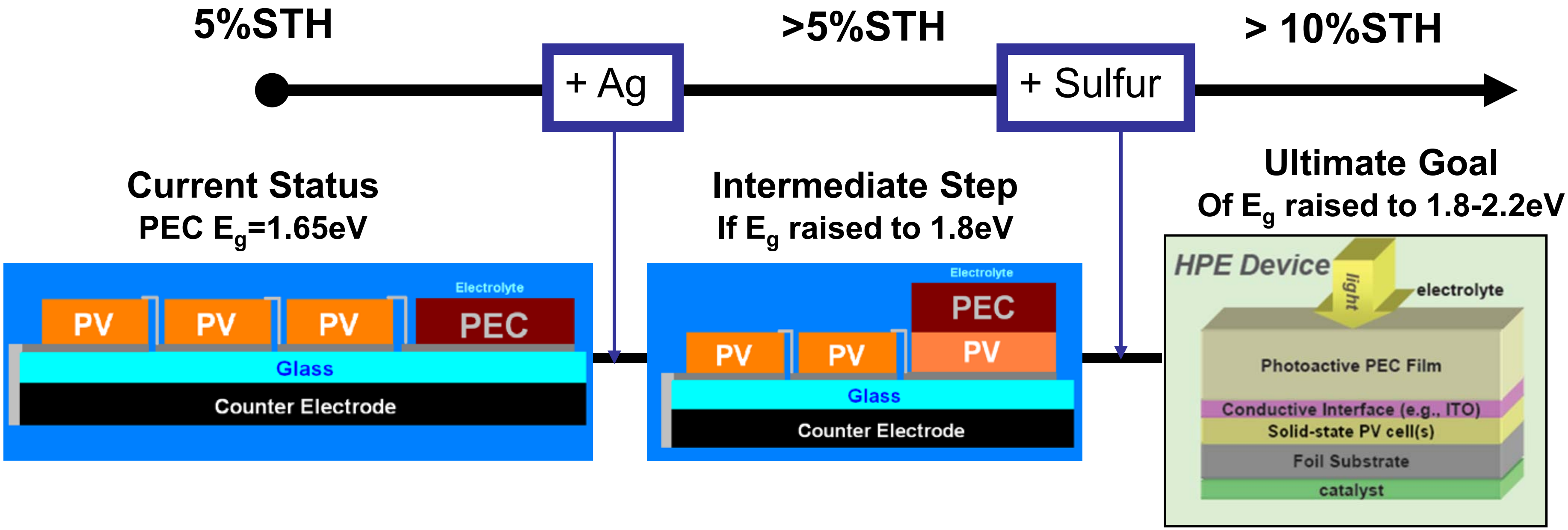
Full Co-Planar Device Operation Using CIGS2 PEC Cell and CIGSe2 Triple-PV Cell

Future Work (I-III-VI$_2$ hybrid photoelectrode)

- **Coplanar Device utilizing 3 PV cells of suitable performance can surpass 5% STH.**
- **Lowering the valence band to increase E_g and decrease overpotential is THE key to high performance chalcopyrite-based PEC hybrid devices.**

Lower overpotential --> fewer PV cells required --> diminishes photocurrent division

Higher band gap: buried PV cell approach possible (synergy with ongoing research in PV industry towards tandem CIGSe-based PV cells)



5%STH

+ Ag

>5%STH

+ Sulfur

> 10%STH

Current Status

PEC E_g=1.65eV

Intermediate Step

If E_g raised to 1.8eV

Ultimate Goal

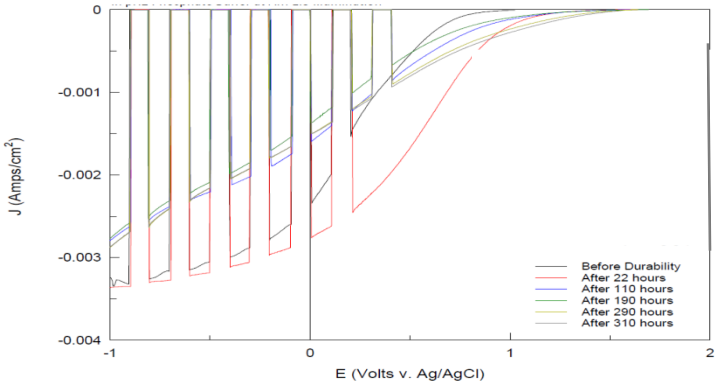
Of E_g raised to 1.8-2.2eV

Durability test

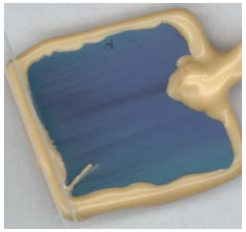
Addressing "Z"

a-SiC photoelectrode:

- Under AM1.5G @1mA/cm^2, in pH2 buffer solution.
- Photocurrent initially increases then decreases and stabilizes after 110 hours.
- No dark current increase for 310 hours



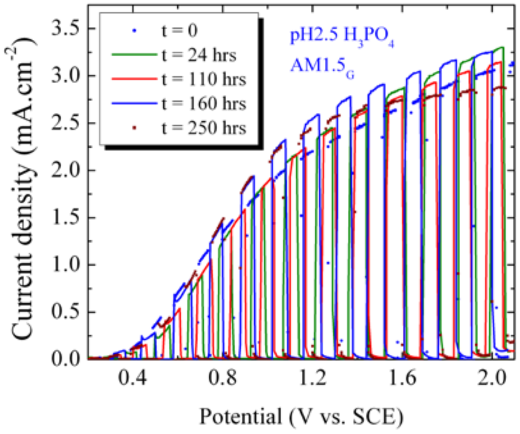
Hybrid PV/a-SiC device after 310-hrs



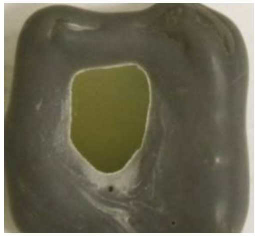
[Data measured by NREL]

WO$_3$ photoelectrode:

- Under AM1.5G @1.8V, in pH2.5 H_3PO_4.
- High corrosion resistance of tungsten oxide in acidic solution for up to 250 hours.

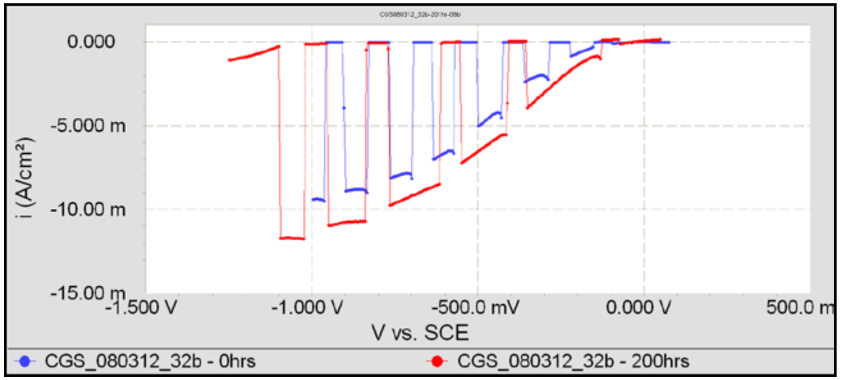


WO$_3$ thin film after 250-hrs

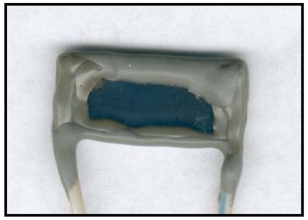


CGSe photoelectrode:

- Under AM1.5G @1.6V, in 0.5M H_2SO_4.
- CGSe$_2$ material performance actually *improved* after operating for 200 hours at >4mA/cm^2.



CGSe thin film after 200-hrs



Collaborations

– *US Department of Energy PEC working group*: Leading task force on WO_3,I-III-VI_2 and a-SiC photoelectrodes

– *National Renewable Energy Laboratory*: collaboration to perform theoretical research and advanced morphological analysis of new materials.

– *University of Nevada at Las Vegas*: collaboration to analyze the surface energy band structure of new photoelectrode materials.

– *University of California in Santa Barbara*: collaboration on surface treatment for catalytic purposes.

– *Stanford University*: collaboration on surface treatment for catalytic purposes.

– *Helmholtz Centre Berlin*: New alloy composition (sulfurization) fabrication, material/device theory

– *International Energy Agency/HIA/Annex 26*: collaboration with international institutes and universities including EMPA (Swiss) and University of Warsaw (Poland).

Project summary

The MVSystems/UH project is accelerating the development of **three important PEC thin-film materials classes** (a-SiC, WO_3 and CGSe) with high potential for **Cost-Effective 2nd Generation PEC Devices.**

Z - Durability

→ At least 200-hrs for each material demonstrated (so far tested)

AC - Device design

→ Monolithic integration demonstrated (a-SiC) or identified (WO_3 and CGSe)

Y - Efficiency

→ Routes to >5% STH outlined for each material class

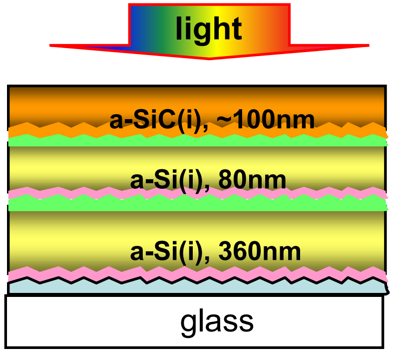
All three material classes have passed Go/NoGo decision in November 2010

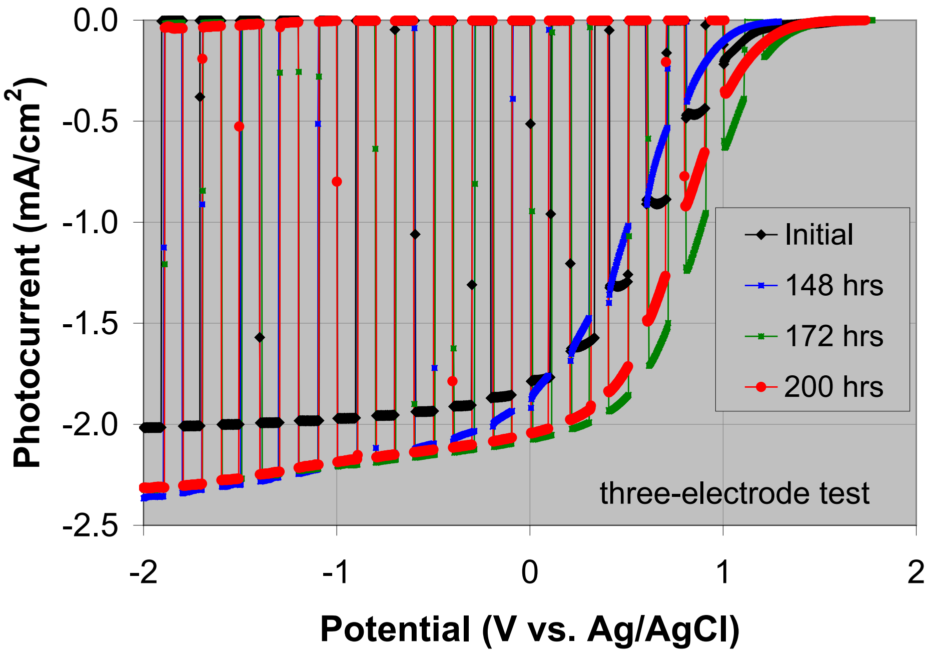
Technical Back-Up Slides

Progress: Corrosion resistance up to 200 hrs

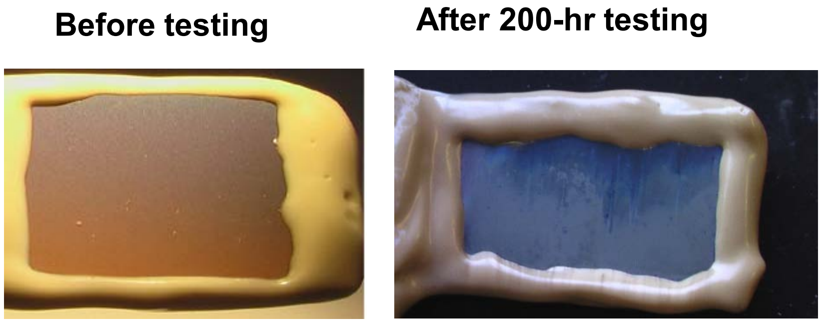
Test conditions:

- **Sample tested:** *hybrid PEC cell*
- **Counter electrode:** *Pt*
- **Electrolyte:** *buffer pH2 (sulphamic acid solution with added potassium biphthalate)*
- **Current bias:** *1.6 mA/cm^2*





Current vs. potential (before and after test)

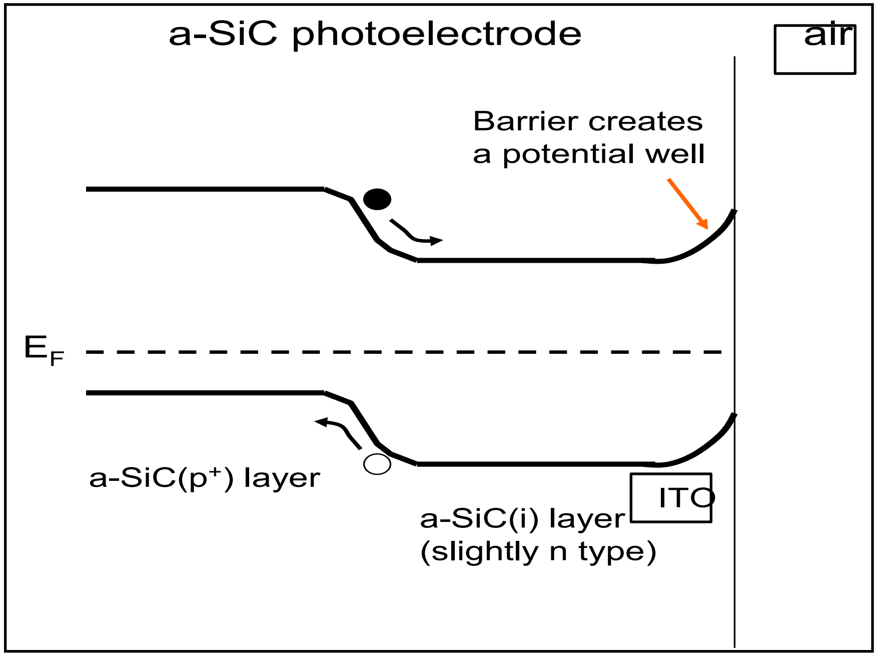


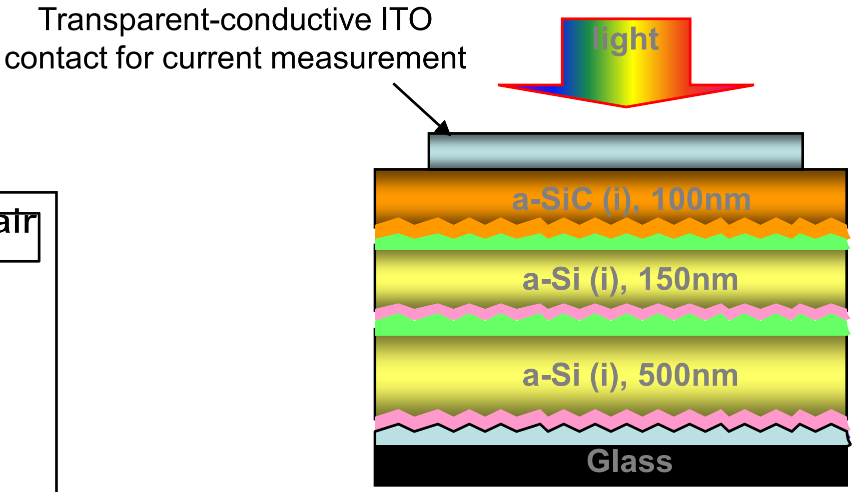
- H_2 production throughout the test
- No degradation during durability/corrosion test for 200 hours (So far)

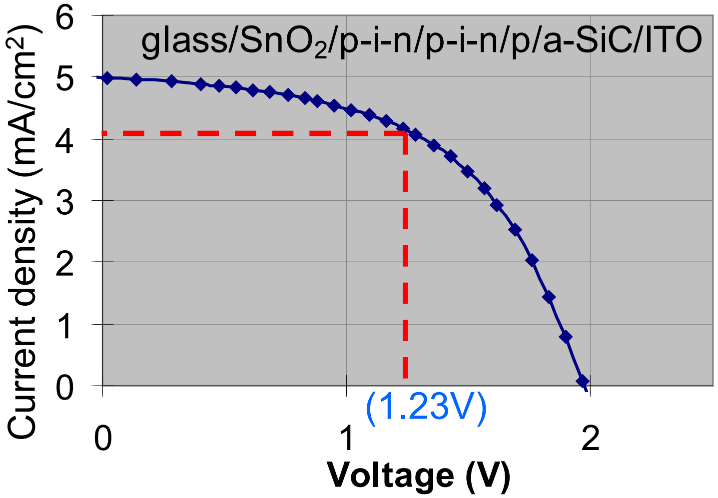
[Data measured by NREL]

a-SiC: Barrier at a-SiC/ITO interface

Solid state device has a barrier
at the a-SiC /ITO interface



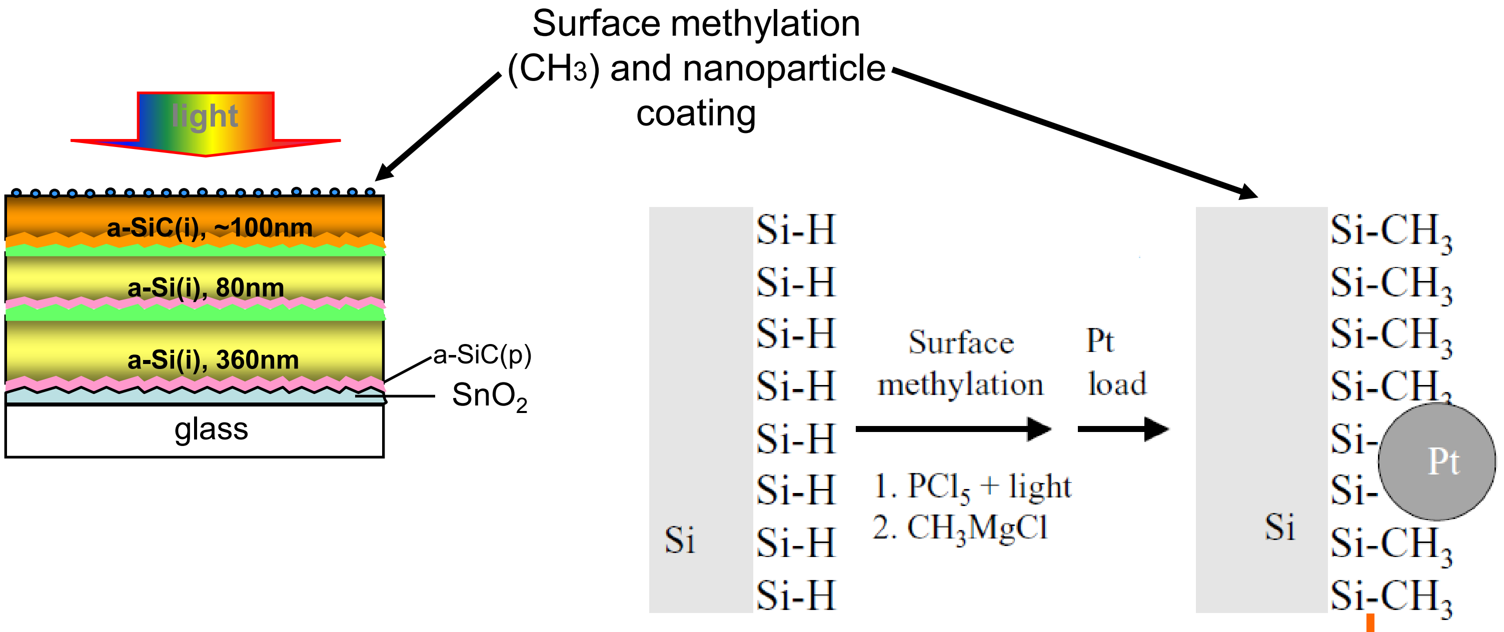

Transparent-conductive ITO contact for current measurement



Hence current density is low (~4mA/cm^2)
and FF is low
Despite this we can still get 4mA/cm^2
Which could translate to STH >5%

Removal of barrier will improve the solid state device substantially

a-SiC: Surface methylation and nanoparticles


Surface methylation (CH_3) and nanoparticle coating

CH_3-termination (methylation) prevents oxidation

Photocurrent enhanced

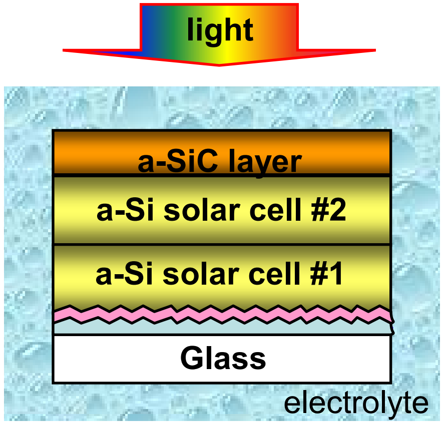
(i.e., from 5 to 25 mA/cm^2 in n-Si electrode*)

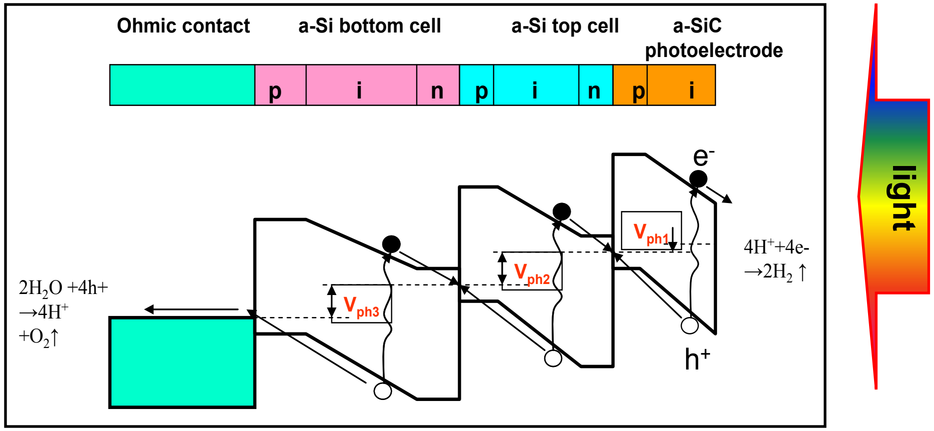
* Takabayashi, Nakamura, & Nakato, Journal of Photochemistry & Photobiology A, 166 (2004).

a-SiC: Hybrid PV/a-SiC PEC Device - Simulation Results

Addressing "Y"

- Energy band diagram for hybrid PV/a-SiC PEC device





- Calculated photocurrent and STH efficiency for 3 different configurations:

Photo-electrode	Eg (eV)	Jsc (mA/cm^2) Available	Voc (V)	PV cell configuration	Filtered Available	Voc (V)	STH (%) Possible
a-SiC:H (1)	2	8.85 (100 nm)	0.6 (p-i)	a-Si/a-Si (620nm/132nm)	7.1	1.9	8.73
a-SiC:H (2)	2	8.85 (100 nm)	0.6 (p-i)	nc-Si/a-Si (1.5µm/244nm)	8.85	1.5	10.89
a-SiC:H (3)	2	12 (250 nm)	>1 (p-i-n)	nc-Si (1.5µm)	12.0	0.6	14.7

STH eff. >10%