

# 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

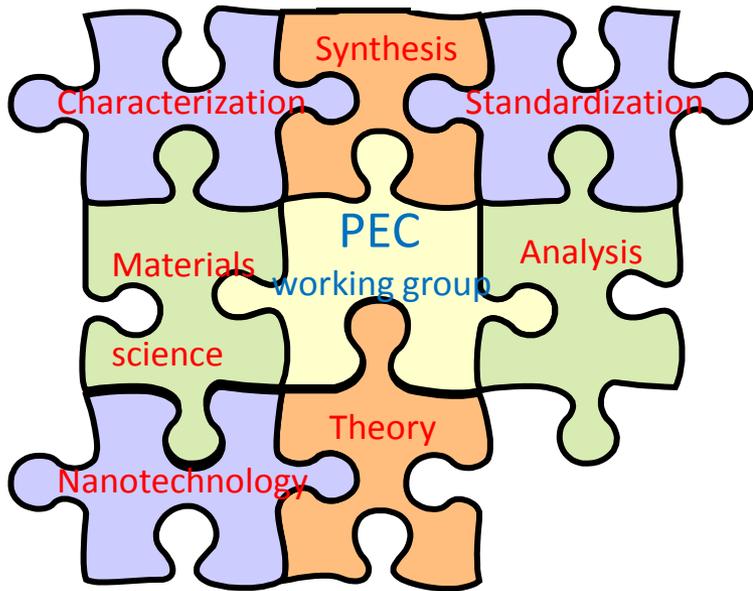
- Total project funding
  - DOE share: \$2,970,172
  - Contractor share: \$820,000

## 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.



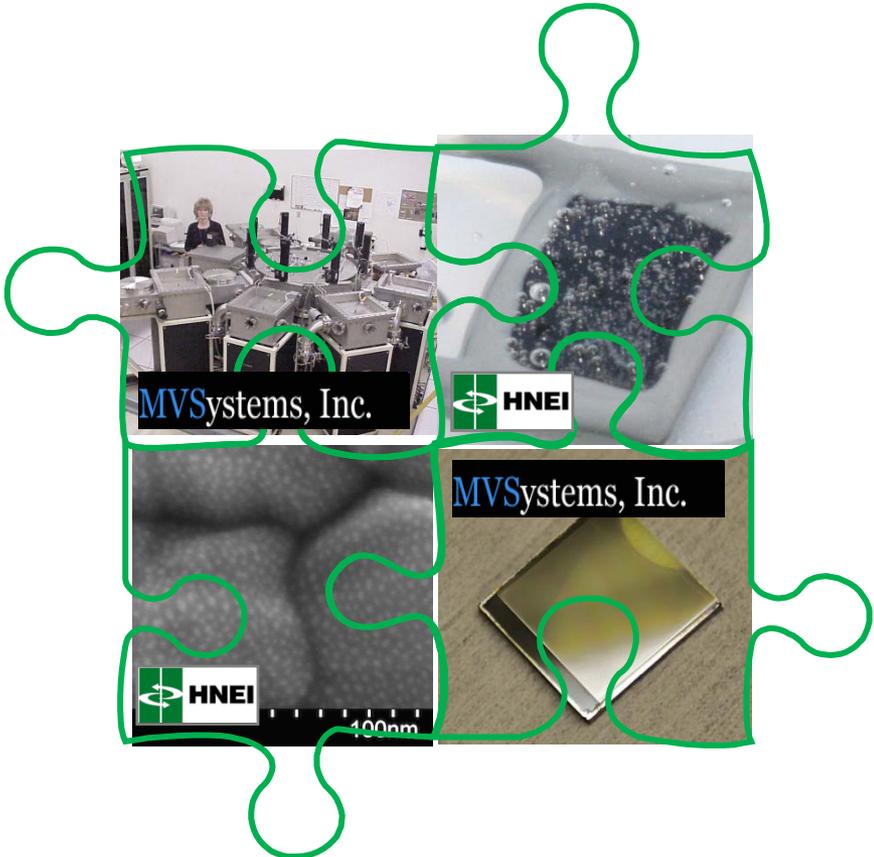
**PEC Working Group:**  
 Evaluating working directions  
 Sharing and building-up knowledge  
 Accelerating research progress

➤ **Thin-Film Materials for Cost-Effective 2<sup>nd</sup> Generation PEC Devices**

- a-SiC
  - WO<sub>3</sub>
  - CGSe
- } **powered by a-Si tandem solar cell**



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



# Relevance - Objectives

3 material classes covered in this project:

- Amorphous silicon carbide (a-SiC)

(performed by MVS)

MVSystems, Inc.

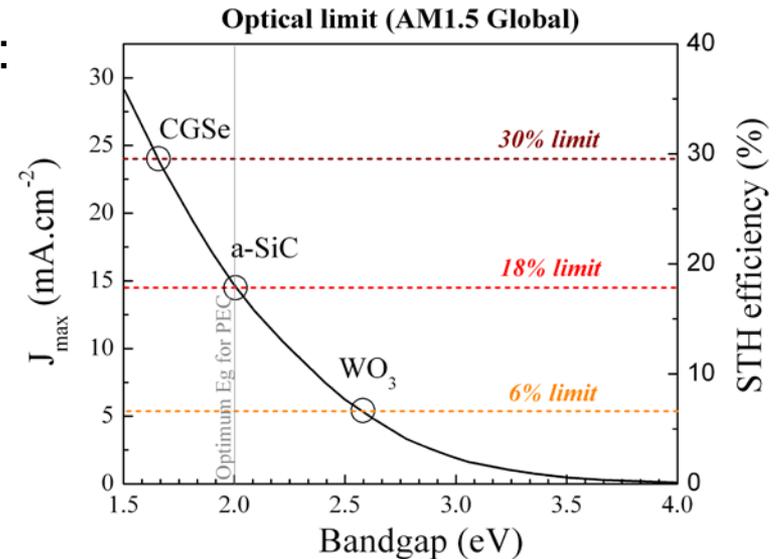
- Tungsten oxide (WO<sub>3</sub>)

(performed by HNEI)

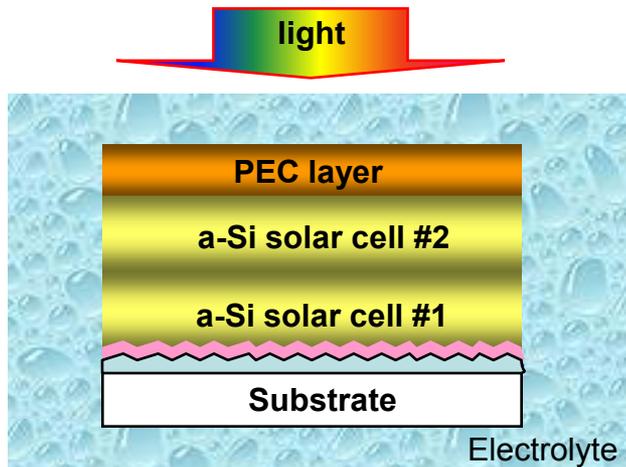


- I-III-VI<sub>2</sub> (Copper Chalcopyrite-based)

(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<sup>2</sup>

Material/Device Durability\*

200hrs

Device Efficiency (STH)

5%

Amorphous Silicon Carbide (a-SiC)

8mA/cm<sup>2</sup>

*>100% Achieved*

310hrs

*>100% Achieved*

1.6%STH

*32% Achieved*

Tungsten Oxide (WO<sub>3</sub>)

3.6mA/cm<sup>2</sup>

*90% Achieved*

250hrs

*>100% Achieved*

3.1%STH

*60% Achieved*

I-III-VI<sub>2</sub>

(Copper Chalcopyrite-based)

20mA/cm<sup>2</sup>

*>>100% Achieved*

200hrs

*100% Achieved*

4.3%STH

*85% Achieved*

\* Test conditions in slide #24.

# Relevance – Barriers

	a-SiC	WO <sub>3</sub>	I-III-VI <sub>2</sub> (Copper Chalcopyrite-based)
<b>AB: Synthesis</b>	Entire PEC device fabricated with low-cost PECVD in a 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)
<b>AC: Device design</b>  - Achieved:  - Barriers:	Monolithic device  <b>No</b>	Hybrid PEC device concept demonstrated with mechanical stack  <b>Current deposition temperature requires innovative integration scheme</b>	Hybrid PEC device concept demonstrated with co-planar PV/PEC  <b>Current deposition temperature requires innovative integration scheme</b>
<b>Z: Durability</b> - Achieved: (so far tested) - Barriers:	310-hrs  <b>No</b>	250-hrs  <b>No</b>	200-hrs  <b>No</b>
<b>Y: Efficiency</b> - Achieved:  - Barriers:	Limited STH (1.6%) compared to the solid state version (>5%)  <b>Need to modify surface to lower overpotential</b>	3.1% STH with pure WO <sub>3</sub> (2.6 eV).  <b>Need to reduce material bandgap to increase light absorption</b>	4.3% STH achieved with co-planar integration.  <b>Need to modify band alignment to lower onset potentials</b>

# 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<sub>3</sub>**: identify stable alloys with appropriate band gap

- decrease bandgap from 2.6~2.8 eV to close to 2.0 eV

**I-III-VI<sub>2</sub>**: 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 (WO<sub>3</sub>) Compounds

Presenter: *Nicolas Gaillard*, Hawaii Natural Energy Institute

Part III

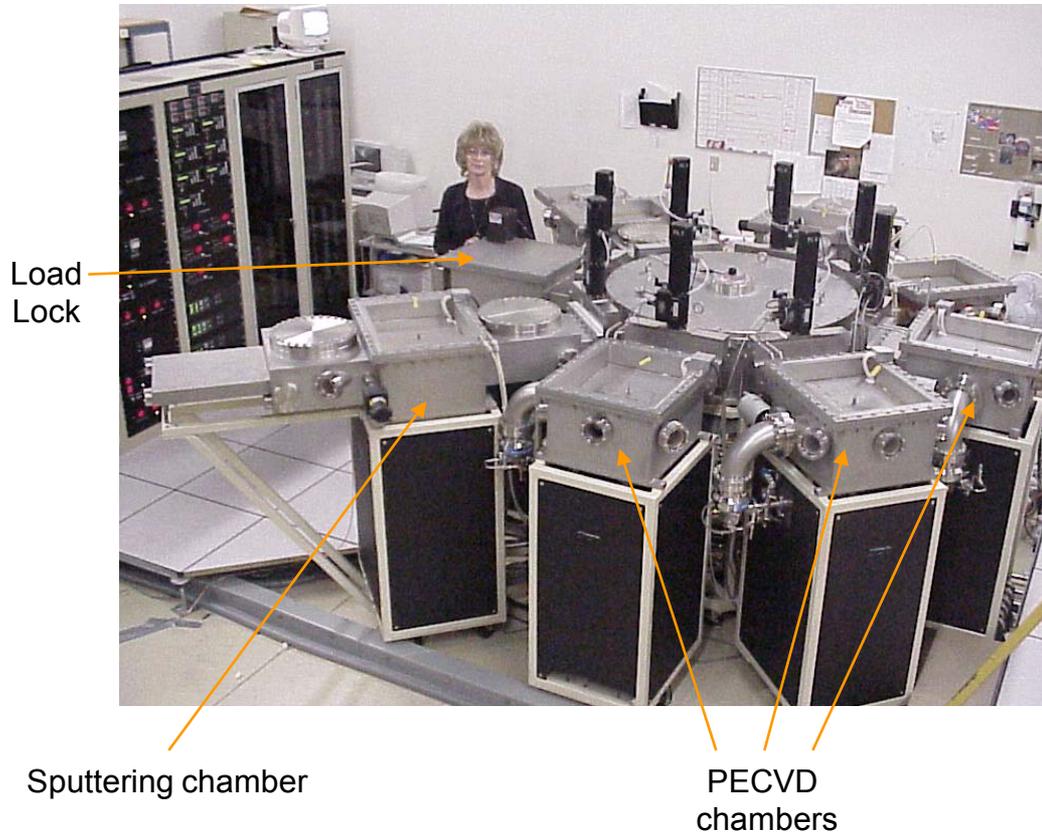
# Copper Chalcopyrites (CIGS)

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.

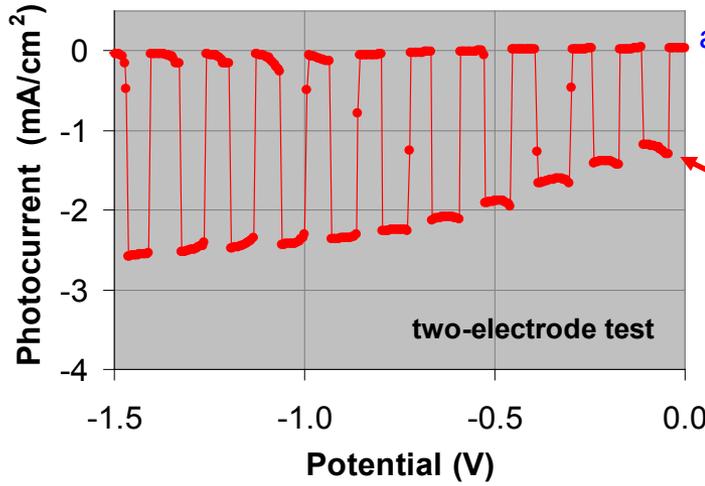
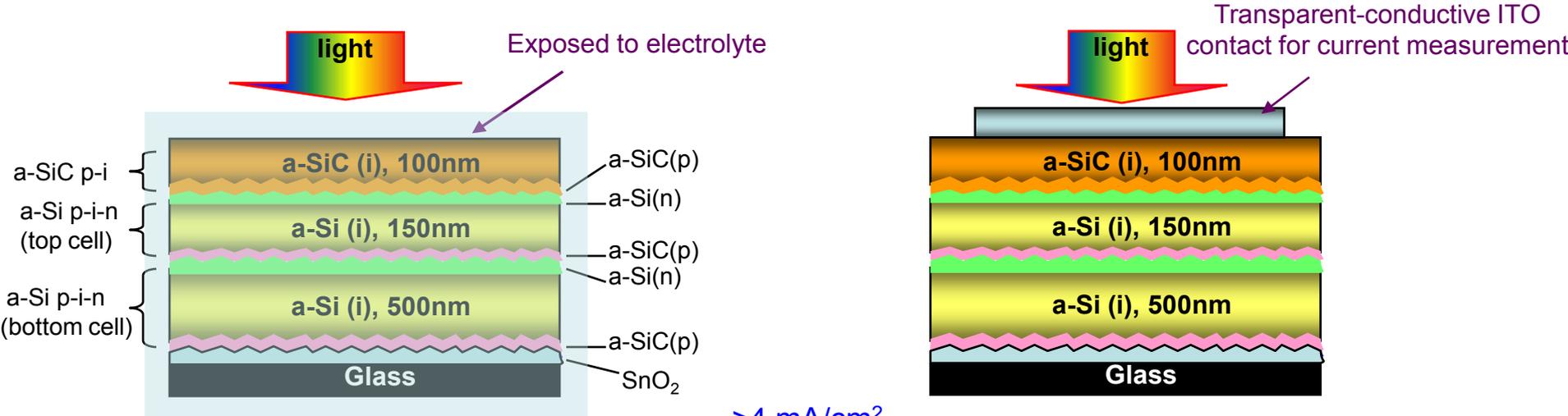


Main deposition parameters:

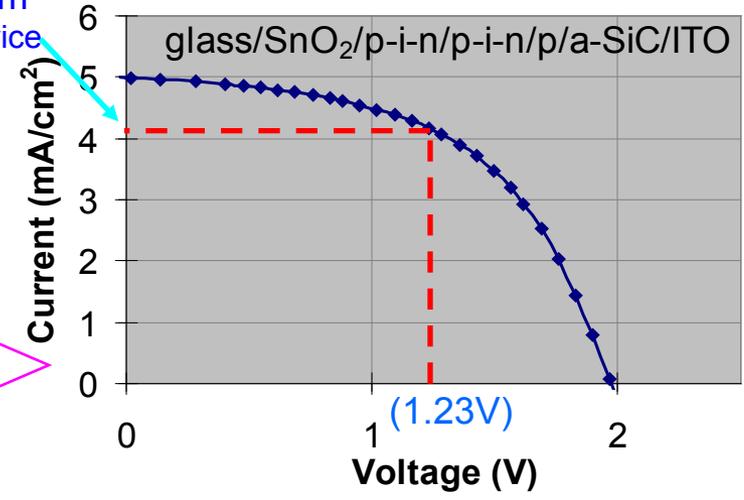
RF power:	10-20 W
Excitation frequency:	13.56 MHz
Pressure:	300-550 mTorr
SiH <sub>4</sub> flow rate:	20 sccm
CH <sub>4</sub> flow rate:	0-20 sccm
H <sub>2</sub> flow rate:	0-100 sccm
Substrate temperature:	200° C

<http://www.mvsystemsinc.com>

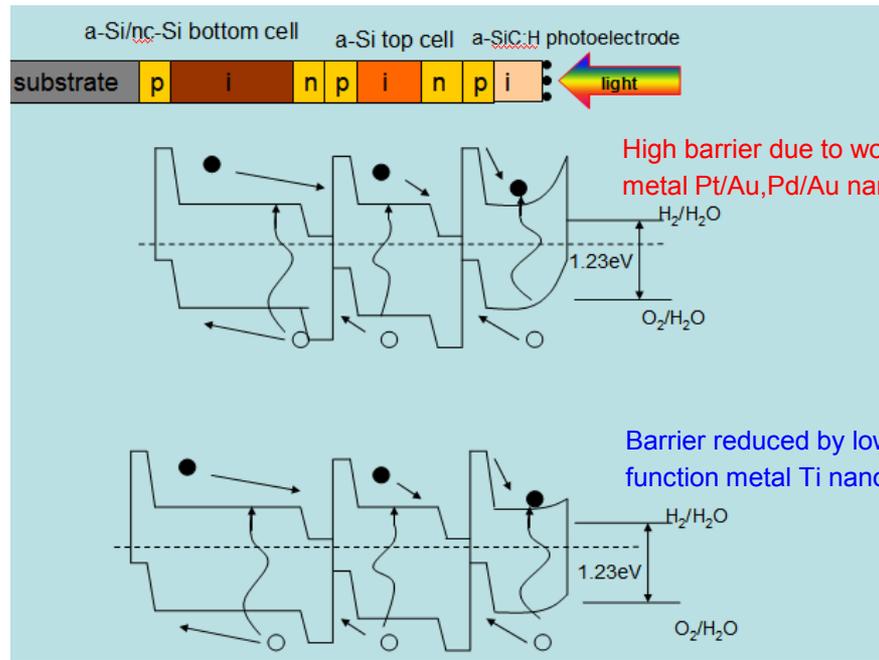
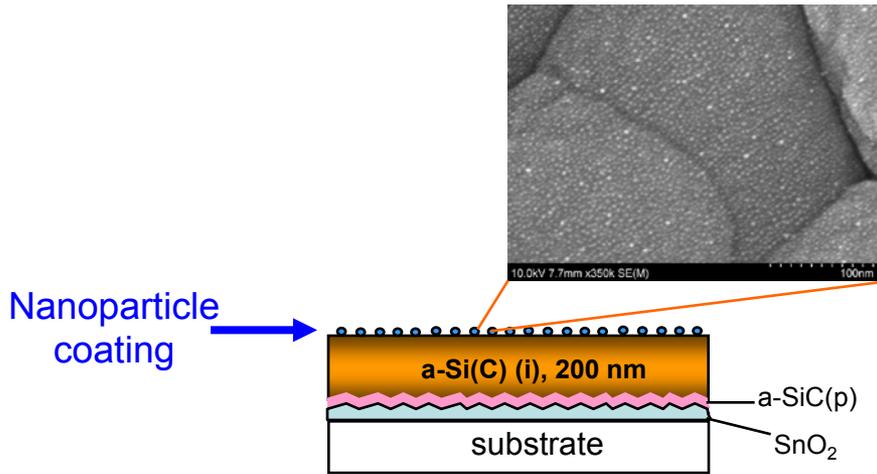
Amorphous and/or nano-crystalline Si solar cells in conjunction with the photo-electrode as the driver for a-SiC, WO<sub>3</sub> and I-III-VI<sub>2</sub> PEC.



>4  $\text{mA}/\text{cm}^2$  as a solid-state device

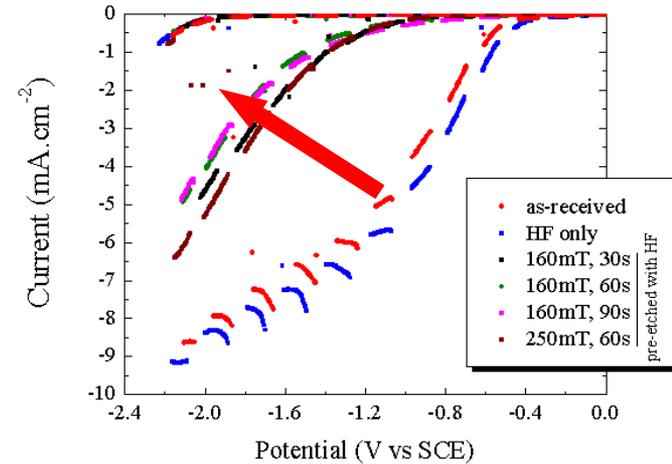


- STH efficiency of hybrid PEC cell should be >6% base on solid state version (right)
- Low current in hybrid PEC cell (left)
- Charge carrier extraction problem at the a-SiC/electrolyte interface

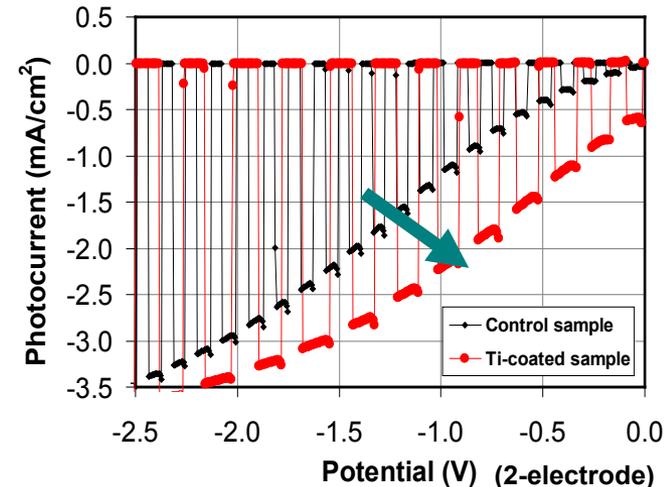


The band diagram at a-SiC/electrolyte interface with high and low work function metal nanoparticle

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



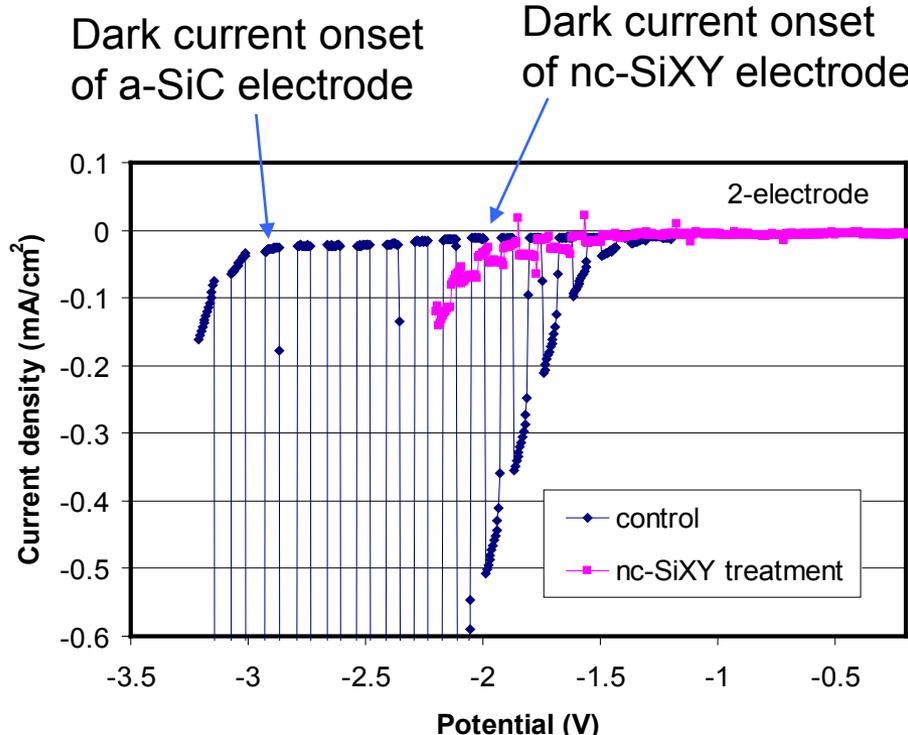
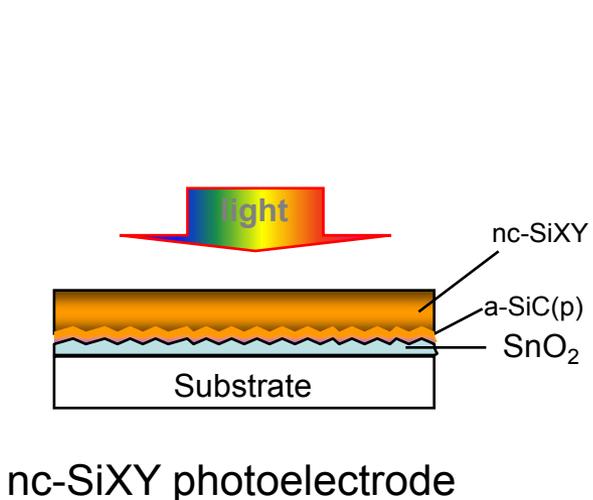
- Low work function material (Ti): increase photocurrent



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

- Develop nanocrystalline Si based thin film for surface modification

Addressing "Y"



## 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).



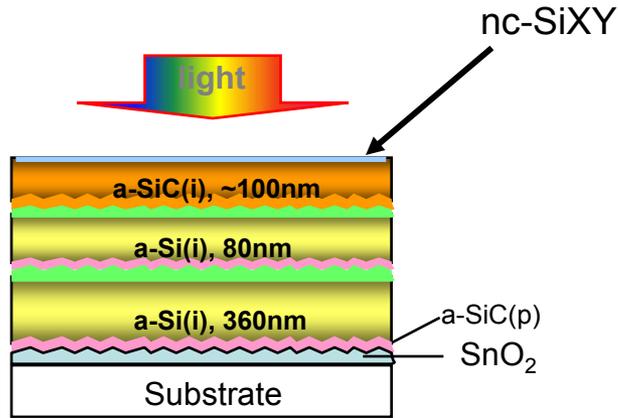
nc-SiXY could be used as a transparent catalyst for HER.

[ Data measured by HNEI ]

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

- Applying nc-SiXY for surface modification

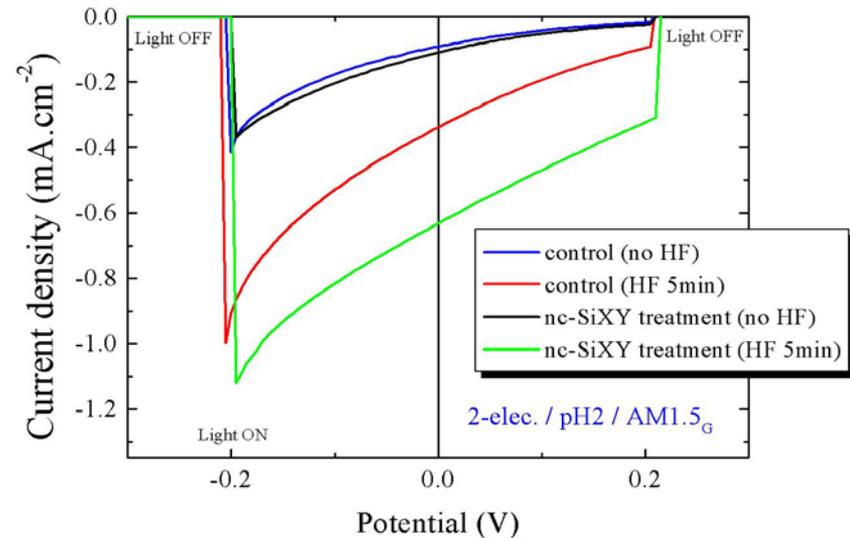
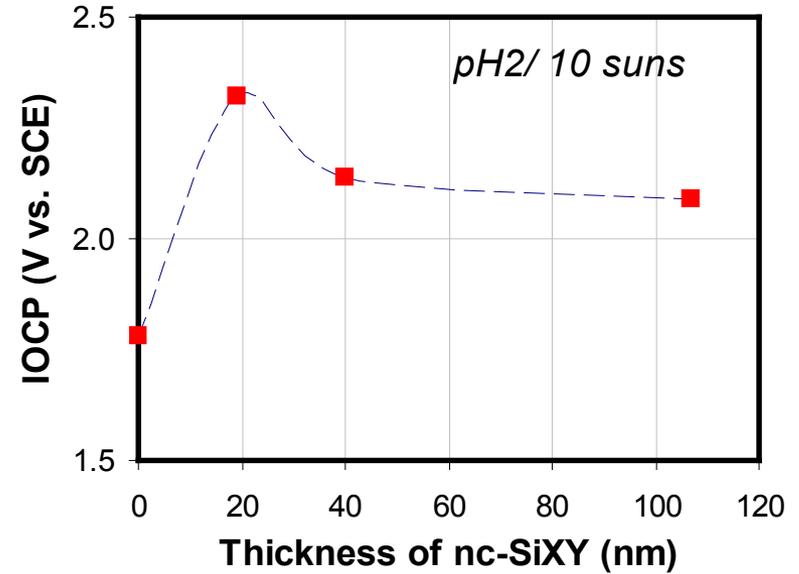
Addressing "Y"



PV/a-SiC hybrid device

Measurement of  $V_{FB}$ : 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<sub>3</sub> 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 (WO<sub>3</sub>) Compounds

Presenter: *Nicolas Gaillard*, Hawaii Natural Energy Institute

Part III

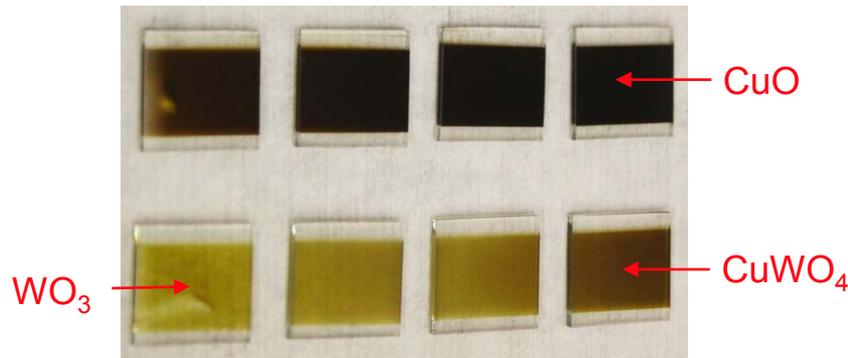
# Copper Chalcopyrites (CIGS)

Presenter: *Nicolas Gaillard*, Hawaii Natural Energy Institute

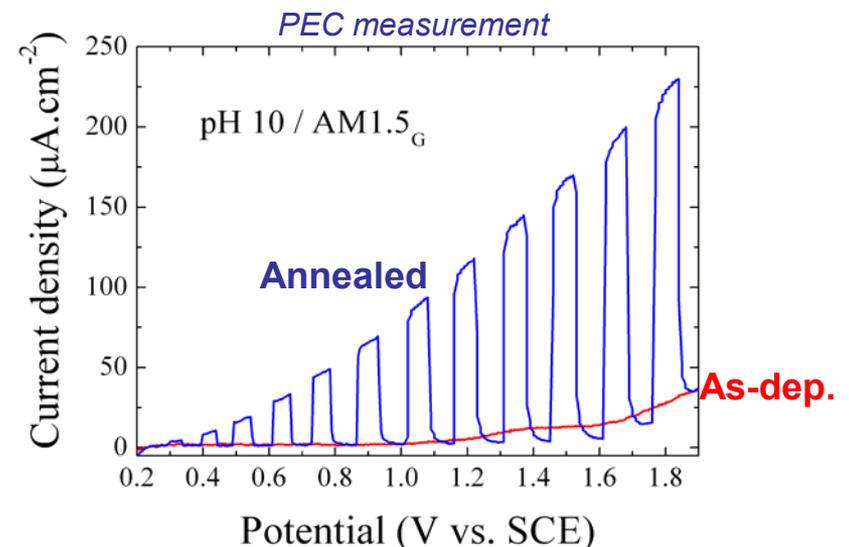
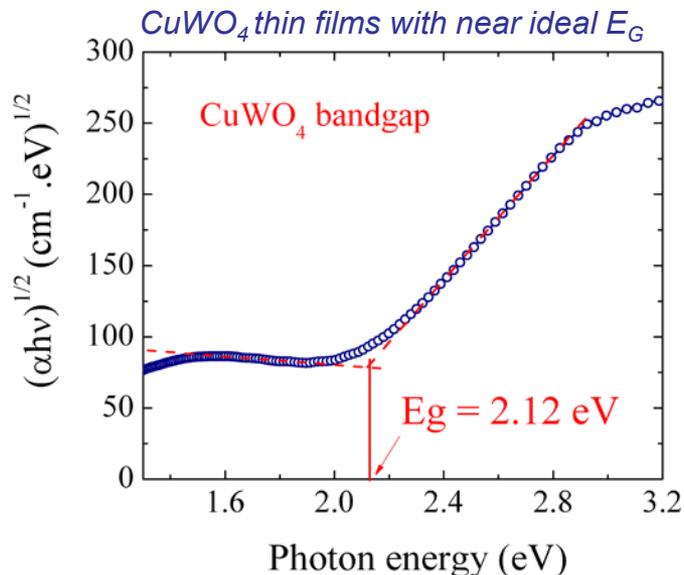
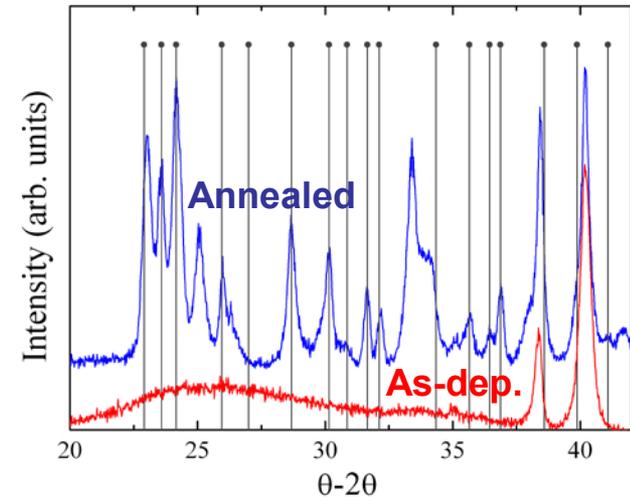
One must identify thermodynamically stable W-based alloys with  $E_g$  close to 2.0 eV

Approach #1:  $\text{CuWO}_4$  "combinatorial" survey using co-sputtering process

$(\text{CuO})_x(\text{WO}_3)_{1-x}$  films obtained by co-sputtering



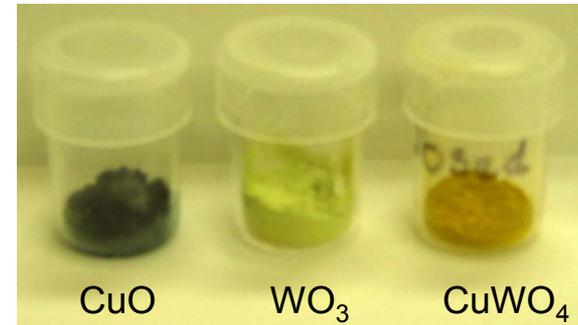
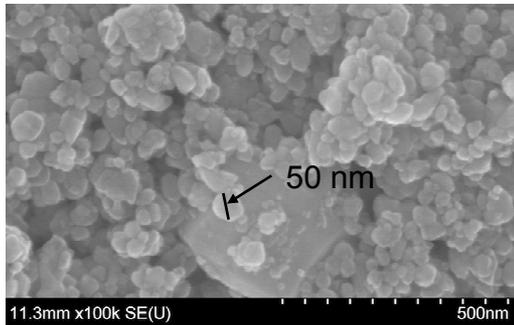
Crystalline  $\text{CuWO}_4$  after 450°C annealing



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

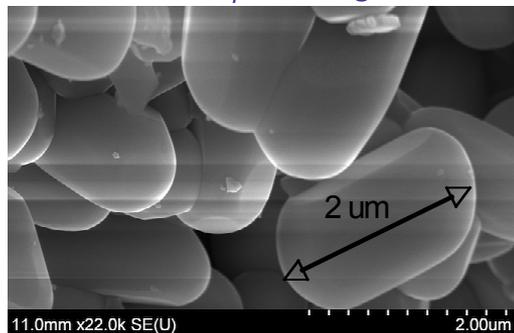
Main advantages over conventional co-sputtering process:

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

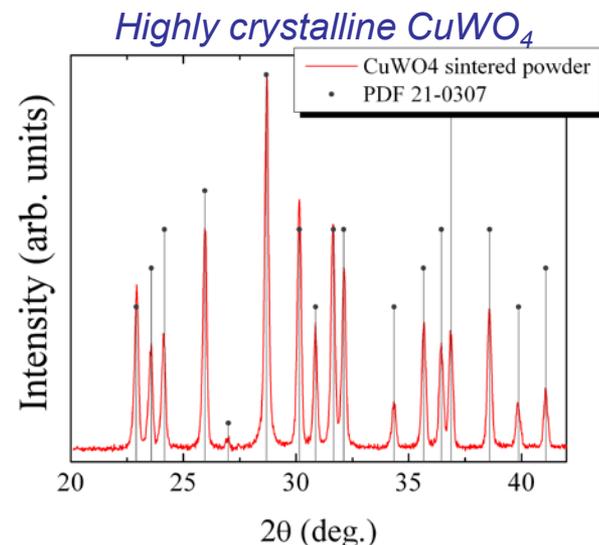


sintering

From  $CuO$  &  $WO_3$  nanopowders...  
... to  $CuWO_4$  micro-grains

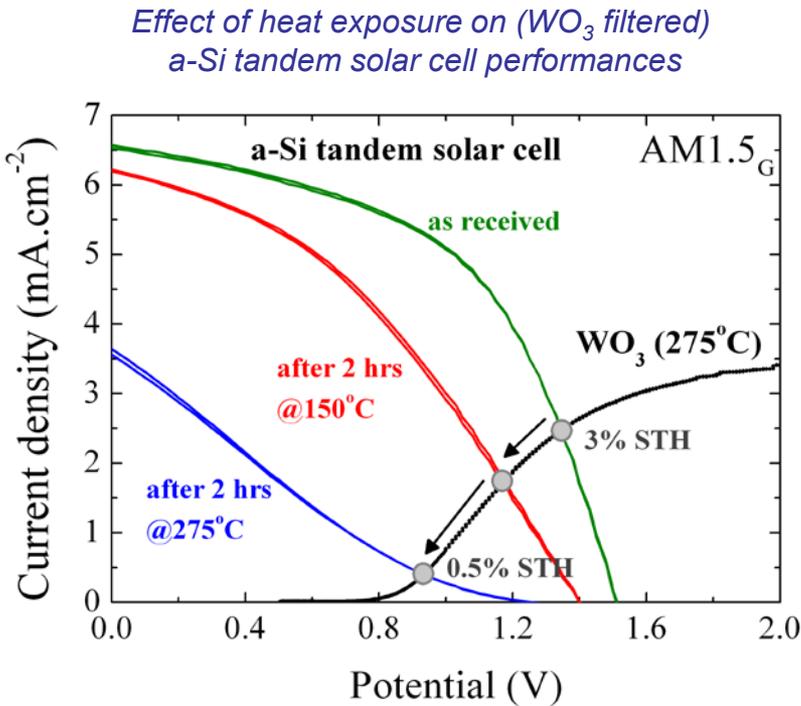


(800°C for 5 hrs)



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

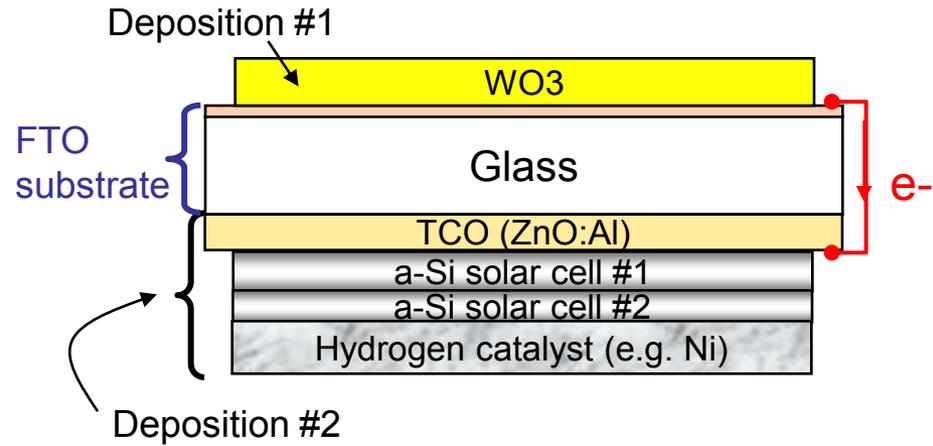
## Issue



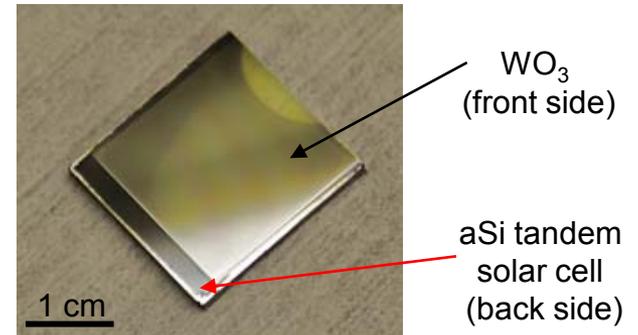
The conventional hybrid PEC electrode approach (with PEC layer deposited on top of solar cells) is not compatible for WO<sub>3</sub> and low-cost a-Si tandem solar cells.

## Solution

Deposition #1: WO<sub>3</sub> on front side  
Deposition #2: inverted a-Si on back side



Picture of PEC hybrid device



# Future Work (WO<sub>3</sub> PEC electrode)

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## Improve the electrical conductivity of CuWO<sub>4</sub> 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<sub>3</sub>-based PEC hybrid device

- Validate the front / back side integration scheme
- Perform extensive indoor and outdoor test with H<sub>2</sub> production quantification.

Part I

# Amorphous Silicon Carbide (a-SiC)

Presenter: *Jian Hu*, MVSystems, Inc

Part II

# Tungsten Oxide (WO<sub>3</sub>) Compounds

Presenter: *Nicolas Gaillard*, Hawaii Natural Energy Institute

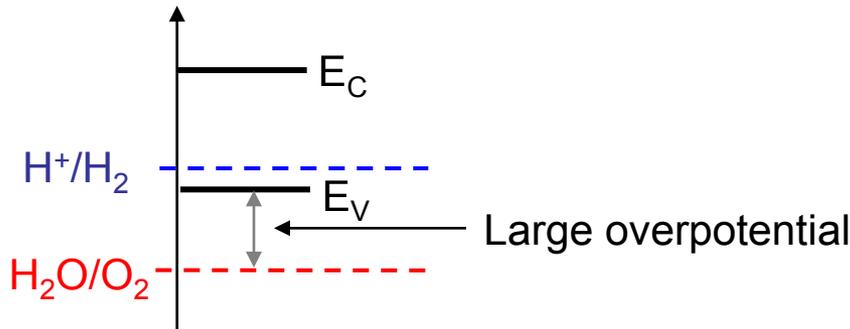
Part III

# Copper Chalcopyrites (CIGS)

Presenter: *Nicolas Gaillard*, Hawaii Natural Energy Institute

# 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

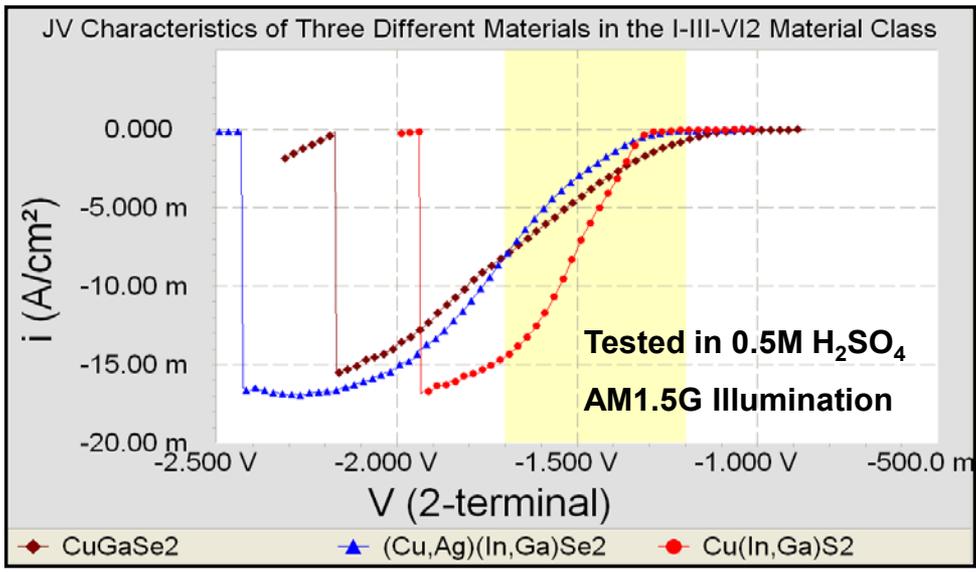
Bandgap:

CuGaSe<sub>2</sub> = 1.65eV (baseline)

(Cu,Ag)(In,Ga)Se<sub>2</sub> up to 1.85eV

Cu(In,Ga)(Se,S)<sub>2</sub> up to 2.43eV

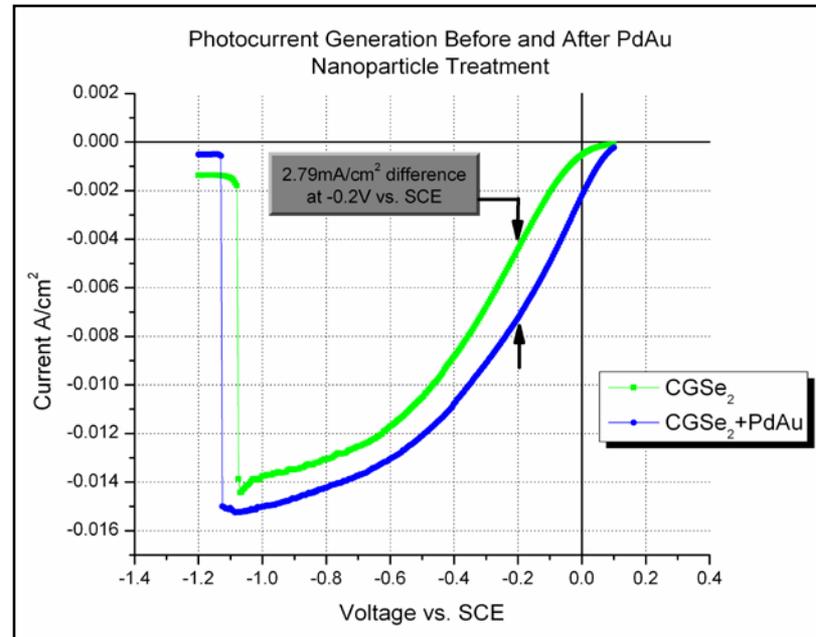
**(Cu<sub>z</sub>Ag<sub>(1-z)</sub>)(In<sub>x</sub>Ga<sub>(1-x)</sub>)(S<sub>y</sub>Se<sub>(1-y)</sub>)<sub>2</sub> alloys are bandgap-tuneable**



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

# Progress: overpotential reduction at CGSe surface

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



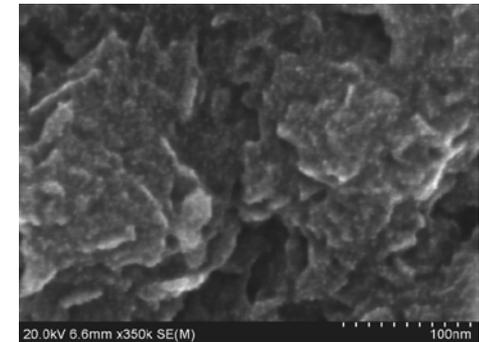
CGSe<sub>2</sub> JV characteristics before and after PdAu nanoparticle deposition showing improvement in "fill factor".

### Effect of Counterelectrode

- RuO<sub>2</sub> is a far superior oxygen-evolution catalyst when used as an anode with I-III-VI<sub>2</sub> photocathodes

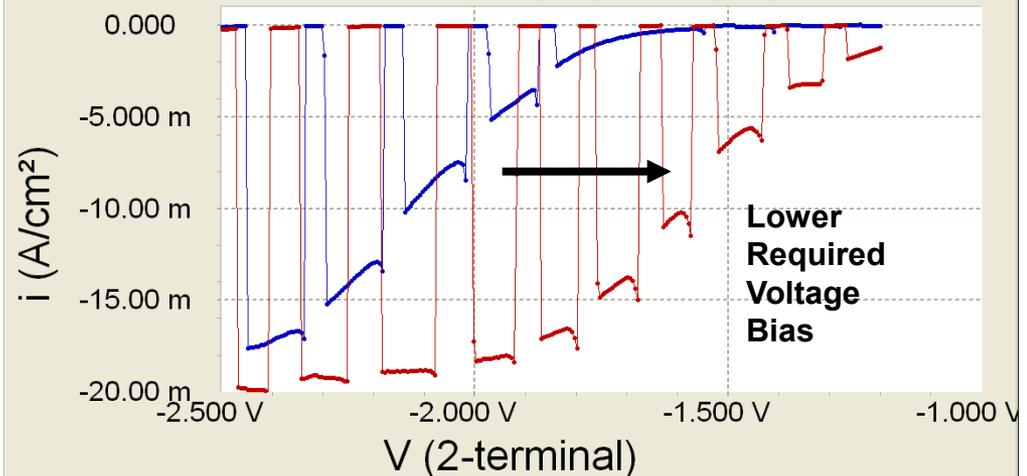
### PdAu nanoparticles (sputtered)

- 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

Comparison of CGSe Measured With a Pt (Blue) or RuO (Red) Counter-Electrode



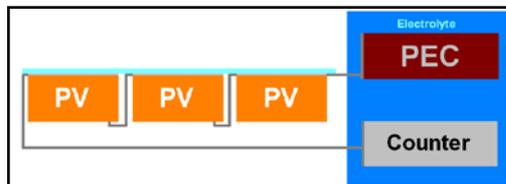
# Progress: STH efficiency with co-planar integration

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

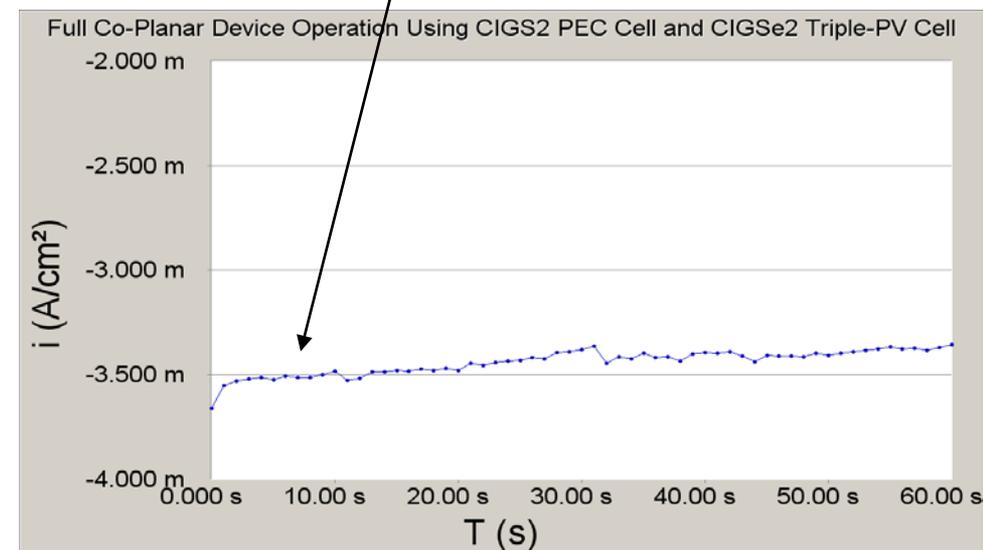
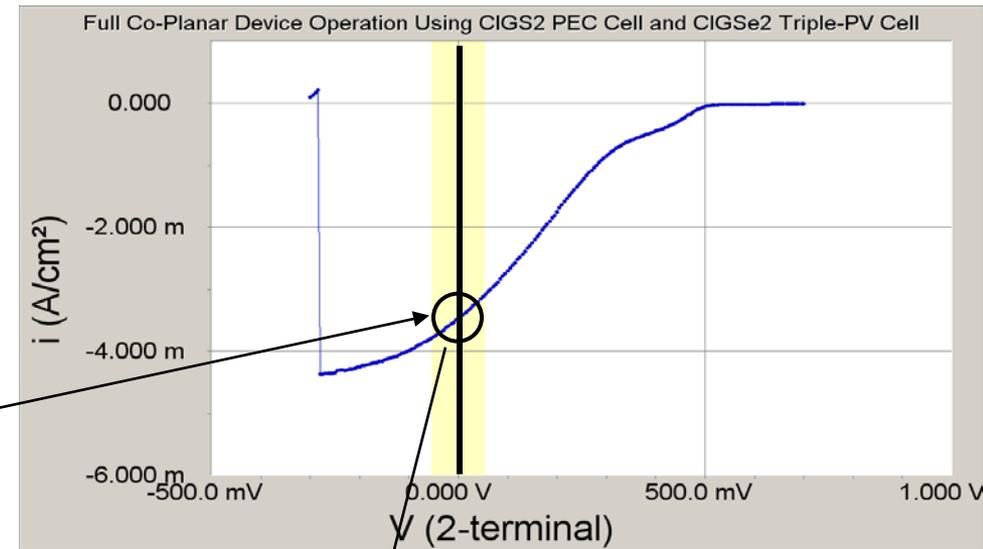
Solution: Large photocurrent produced by materials in this class allow co-planar PV-PEC integration

## 4.3% STH achieved!

- 3 CIGSe<sub>2</sub> PV cells
- CIGS<sub>2</sub> (pure sulfide) PEC
- In a standalone device (no external bias):
  - 3.46mA/cm<sup>2</sup> = 4.3%STH



3 PV + PEC  
serial device



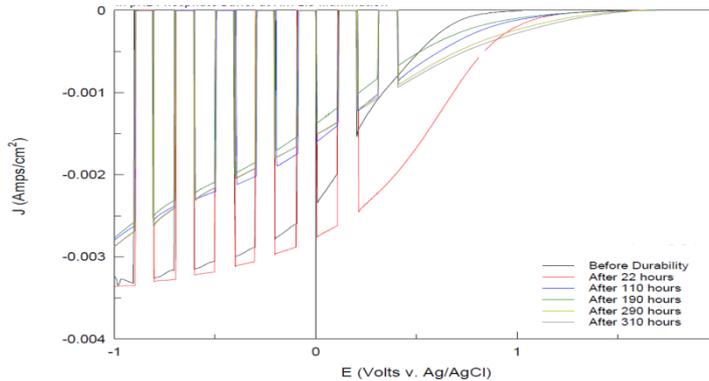


# Durability test

Addressing "Z"

## a-SiC photoelectrode:

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



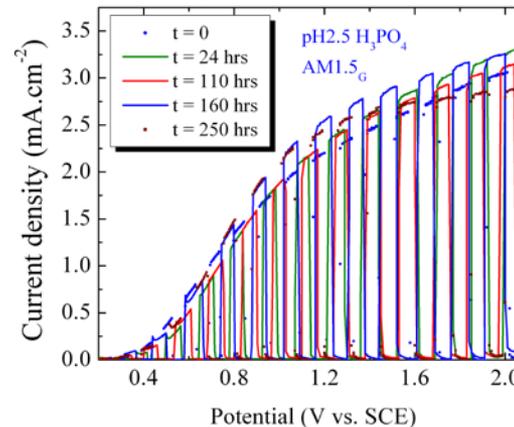
Hybrid PV/a-SiC device after 310-hrs



[ Data measured by NREL ]

## WO<sub>3</sub> photoelectrode:

- Under AM1.5G @1.8V, in pH2.5 H<sub>3</sub>PO<sub>4</sub>.
- High corrosion resistance of tungsten oxide in acidic solution for up to 250 hours.

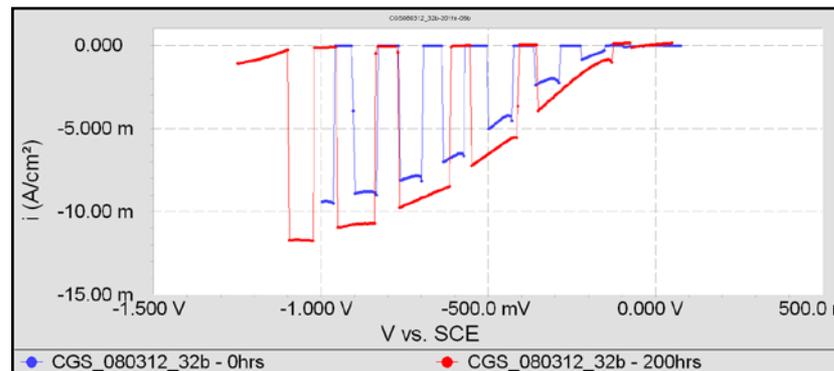


WO<sub>3</sub> thin film after 250-hrs



## CGSe photoelectrode:

- Under AM1.5G @1.6V, in 0.5M H<sub>2</sub>SO<sub>4</sub>.
- CGSe<sub>2</sub> material performance actually *improved* after operating for 200 hours at >4mA/cm<sup>2</sup>.



CGSe thin film after 200-hrs



# Collaborations

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- *US Department of Energy PEC working group*: Leading task force on  $\text{WO}_3$ , I-III-VI<sub>2</sub> 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

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The MVSystems/UH project is accelerating the development of **three important PEC thin-film materials classes** (a-SiC, WO<sub>3</sub> and CGSe) with high potential for **Cost-Effective 2<sup>nd</sup> 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<sub>3</sub> and CGSe)

## Y - Efficiency

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

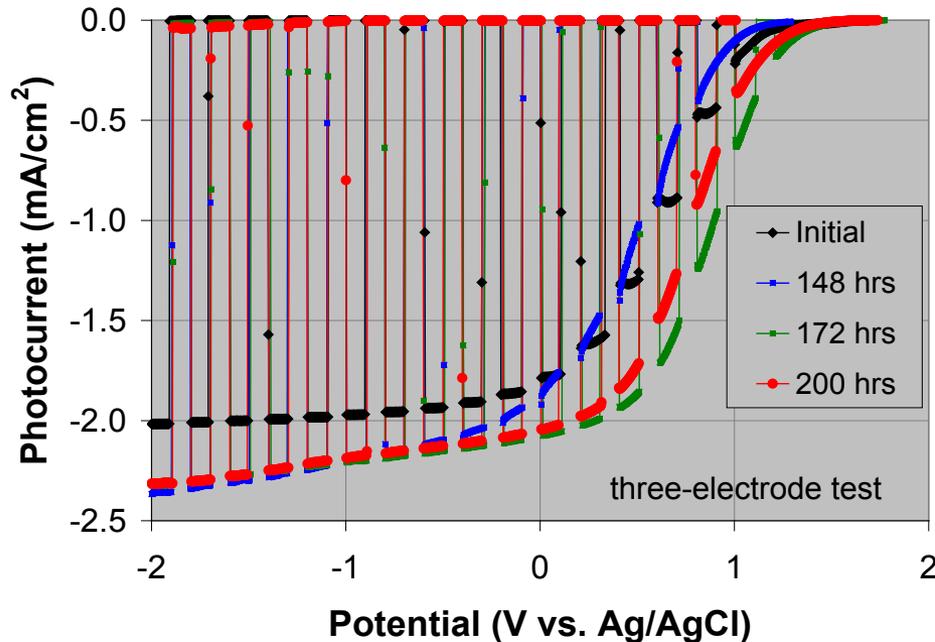
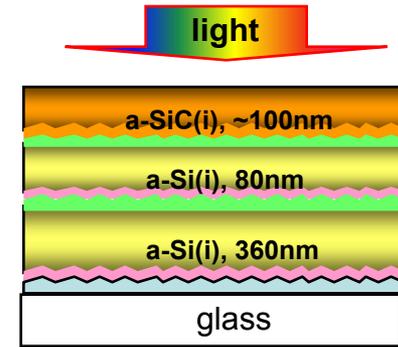
**All three material classes have passed Go/NoGo decision in November 2010**

# 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<sup>2</sup>*



Before testing



After 200-hr testing

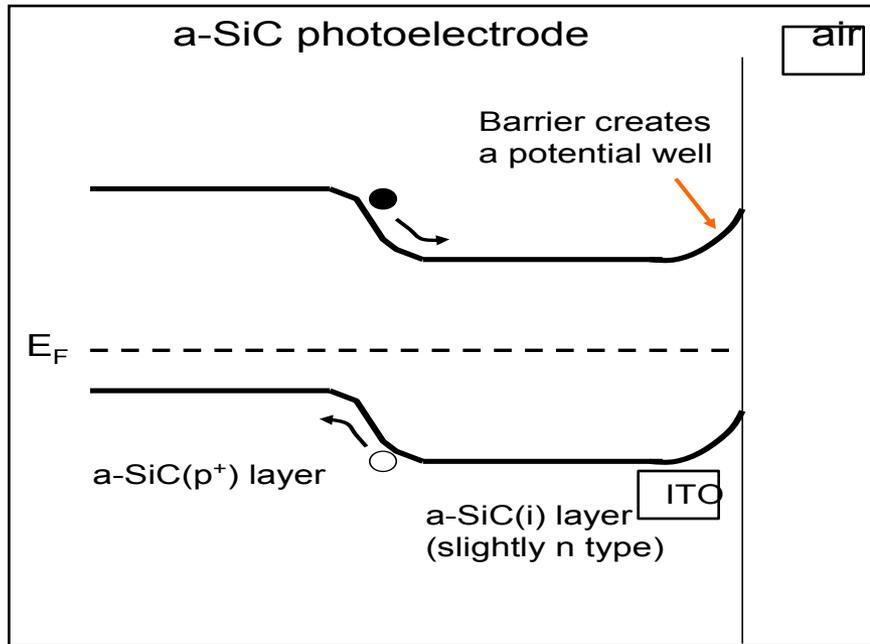


- H<sub>2</sub> production throughout the test
- No degradation during durability/corrosion test for 200 hours (So far)

Current vs. potential (before and after test)

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

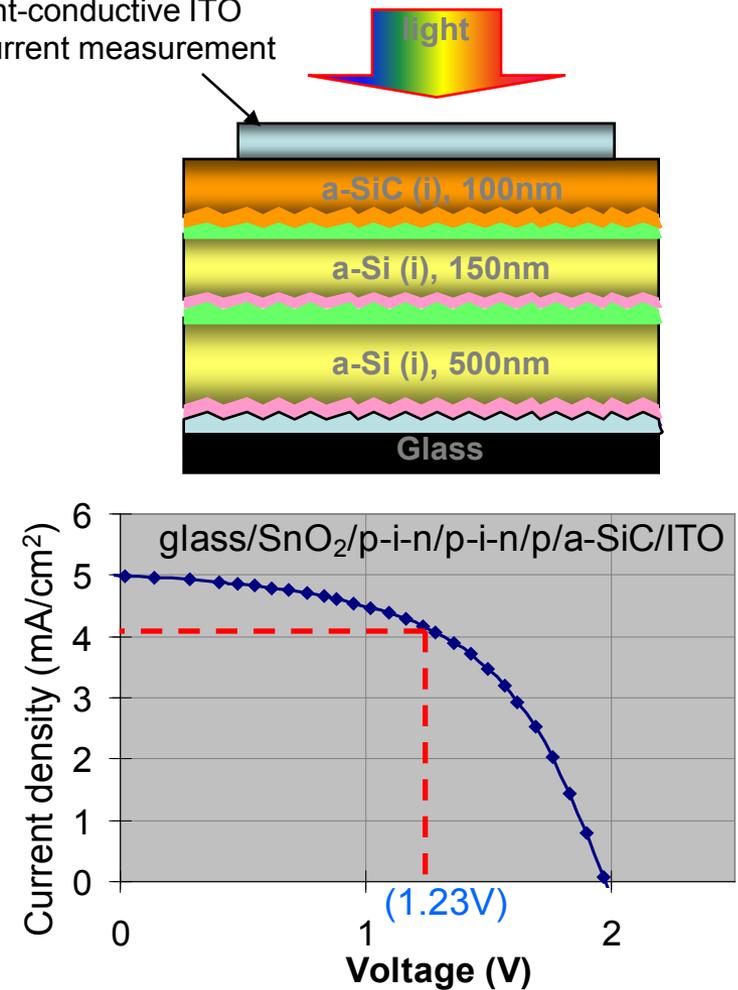
Solid state device has a barrier at the a-SiC /ITO interface



Hence current density is low ( $\sim 4\text{mA/cm}^2$ ) and FF is low

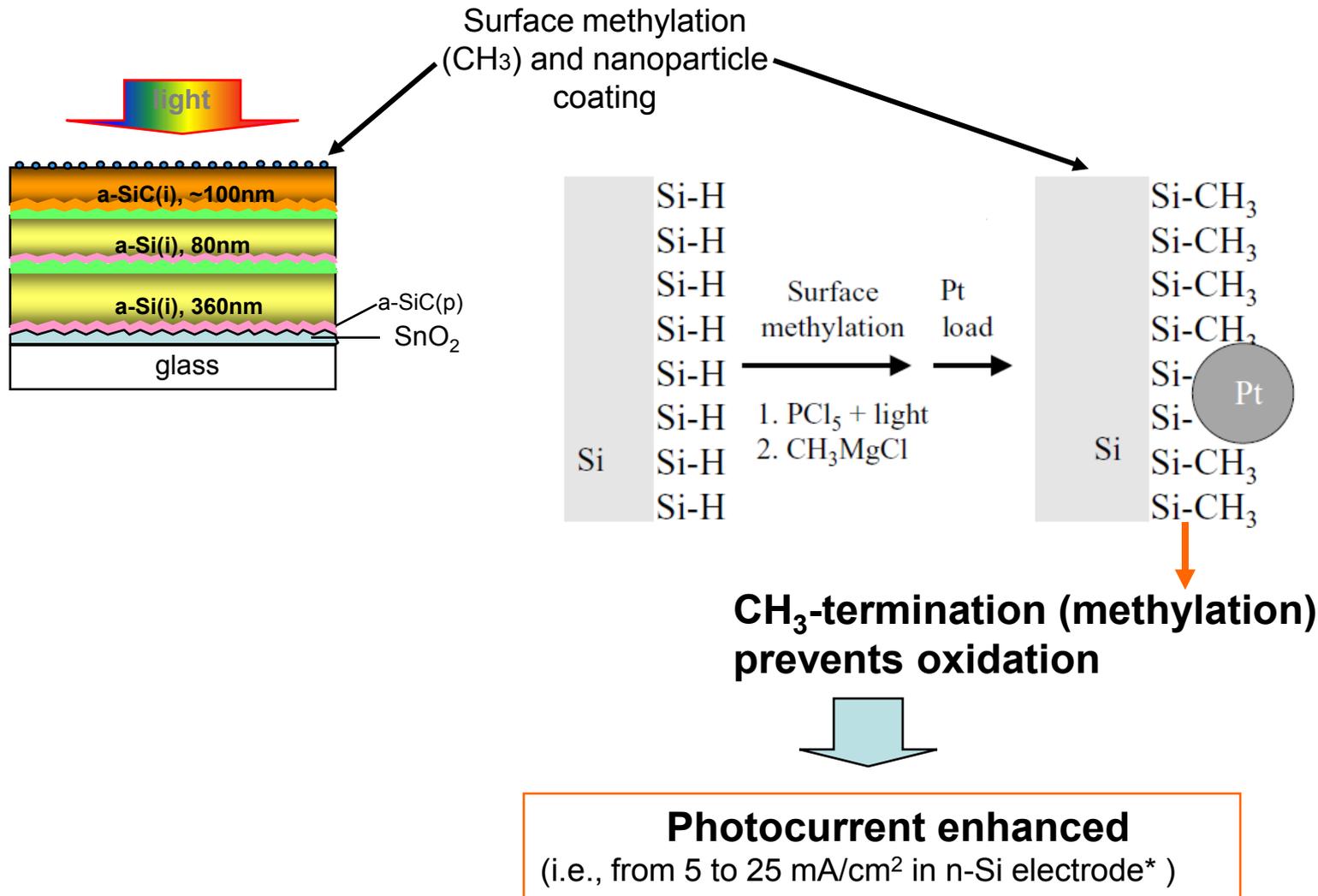
Despite this we can still get  $4\text{mA/cm}^2$  Which could translate to  $\text{STH} > 5\%$

Transparent-conductive ITO contact for current measurement



Removal of barrier will improve the solid state device substantially

# a-SiC: Surface methylation and nanoparticles

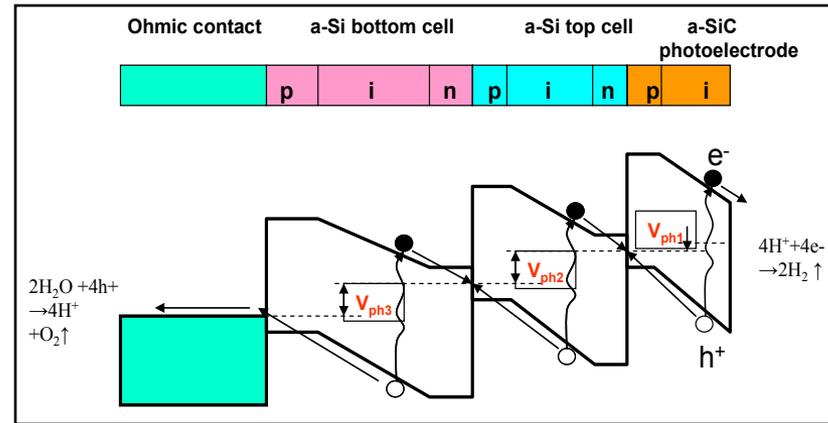
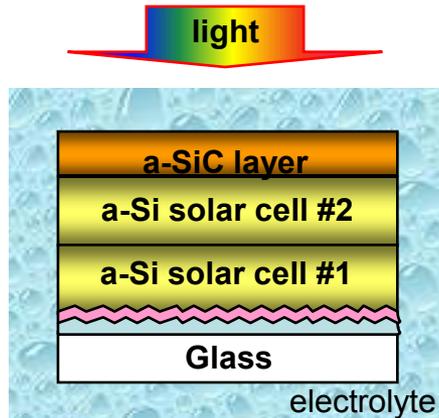


\* Takabayashi, Nakamura, & Nakato, Journal of Photochemistry & Photobiology A, 166 (2004).

# 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 <sup>2</sup> ) 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%