PDP_04_Madan

PHOTOELECTREMICAL HYDROGEN PRODUCTION

Arun Madan
MVSystems, Inc.
May 19, 2009

DE-FC36-07GO17105

Overview

Timeline

- Project start date: 9/1/2007
- Project end date: 8/31/2009
- Percent complete: ~65%

Budget

- Total project funding*
  - DOE share: $**1,358,827**
  - Contractor share: $**339,707**
- Funding received in FY08
- Funding for FY09: $150,000

** funds cover work reported in posters PDP04, PDP05, and PDP06*

Barriers

•Barriers for photoelectrochemical hydrogen production technologies:

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

Partners

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

Overview

poster #PDP04
Progress in the Study of ***Amorphous Silicon Carbide***
as a Photoelectrode in Photoelectrochemical Cells

poster #PDP05
Progress in the Study of ***Tungsten Oxide Compounds***
as Photoelectrodes in Photoelectrochemical Cells

poster #PDP06
Progress in the Study of ***Copper Chalcopyrites*** as
Photoelectrodes in Photoelectrochemical Cells

poster #PDP04

Progress in the Study of Amorphous Silicon Carbide (a-SiC) as a Photoelectrode in Photoelectrochemical (PEC) Cells

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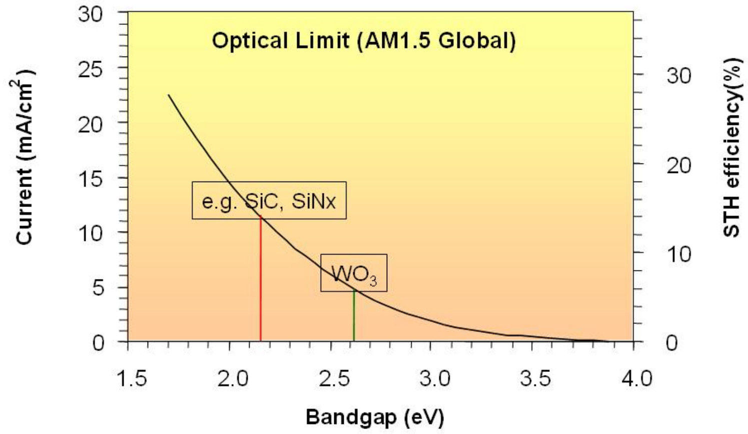
Relevance-Objectives

Advantages of a-SiC photolectrode

- ✓ Lower Eg in comparison with WO_3 produces more photocurrent.
- ✓ Eg can be increased with carbon inclusion into the amorphous silicon (a-Si) material.
- ✓ A-SiC uses same deposition technique (PECVD) as a-Si solar cells (or PV).

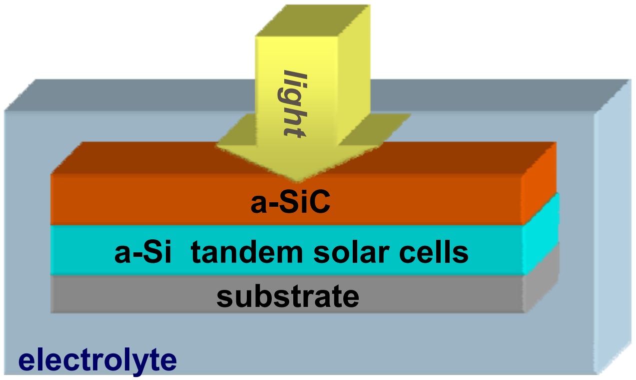


Max current available vs. Bandgap (Eg).

Our goal …

By September, 2009, fabricate the hybrid a-Si tandem solar cell/a-SiC photoelectrode (PV/a-SiC) device which exhibits*,

- photocurrent ≥ 4 mA/cm^2,
- durability in electrolyte ≥ 200 hrs.



Schematic diagram of the PV/a-SiC hybrid device.

**From "Statement of Project Objective", DE-FG36-07GO17105, Attachment #5.*

Relevance-Milestones

Program targets		a-SiC progress status
Year 1: (10/2007----9/2008)		
✓ Material photocurrent ≥ 3 mA/cm^2	100% @ 1/2008	7-8 mA/cm^2 demonstrated with a-SiC-based PEC electrode
✓ durability 100 hrs	100% @ 6/2008	
Year 2: (10/2008----10/2009)		
✓ Material photocurrent ≥ 4 mA/cm^2	100% @ 1/2008	7-8 mA/cm^2 demonstrated with a-SiC-based PEC electrode
✓ Durability: 200 hrs	75% @ 2/2009	durability for up to 150 hrs.
✓ Device STH efficiency ≥ 5%	20% @ 11/2008	1% efficiency achieved with hybrid device (~ 0.83 mA/cm^2).

(Towards the end of Year 2, a GO/NO-GO DECISION evaluation will be performed)

Future: Device optimization

- Photocurrent of 5 mA/cm^2 over 300 hrs; cluster-tool fabrication on extended area flexible substrates
- Photocurrent of 6 mA/cm^2 over 500 hrs; PEC prototype devices: 7.5% STH efficiency over 500 hours

Relevance-Barriers

Barrier	Challenges	Strengths
Y. Materials Efficiency	The band-edge of the a-SiC may be poorly aligned for practical water splitting.	– Bandgap tuned readily from 2.0 to 2.3eV. – Flatband voltage altered by +1.6V with integrated a-Si tandem solar cell.
Z. Materials Durability	Corrosion and photo-corrosion behavior over extended time periods in a variety of electrolyte.	– Stability up to 100 hour in pH2 electrolyte demonstrated. – Platinum surface treatments enhance stability of a-SiC photoelectrodes on metal substrates.
AC. Device Configuration Designs	Optimized a-Si tandem solar cell needs to be developed to match the photocurrent and photovoltage characteristics of newly-developed a-SiC photoelectrodes.	– Extensive modeling shows the hybrid PEC cell could lead to 10% STH efficiency. – Initial results from the first hybrid PEC cell are promising: 3-5 mA/cm^2 (3-electrode) and ~1 mA/cm^2 (2-electrode) at zero bias.

Approaches

Material to hybrid PEC cell development

a-SiC material → a-SiC photoelectrode → Hybrid PEC device

a-SiC material

- **Bandgap (Eg)**
- **Photosensitivity (σ_L/σ_d)***
- **Defect density (γ)****
- **Bonding configuration (IR)**
- **Device performance (p-i-n solar cells)**

a-SiC photoelectrode

- **Surface band structure (XPS/UPS)**
- **Photocurrent**
- **Flatband voltage**
- **Durability in electrolyte**
- **Surface modification**

Hybrid PEC device

- **Flatband voltage**
- **Photocurrent and STH* efficiency**
- **Durability in electrolyte**
- **Surface modification**

** STH: Solar-to-hydrogen.*

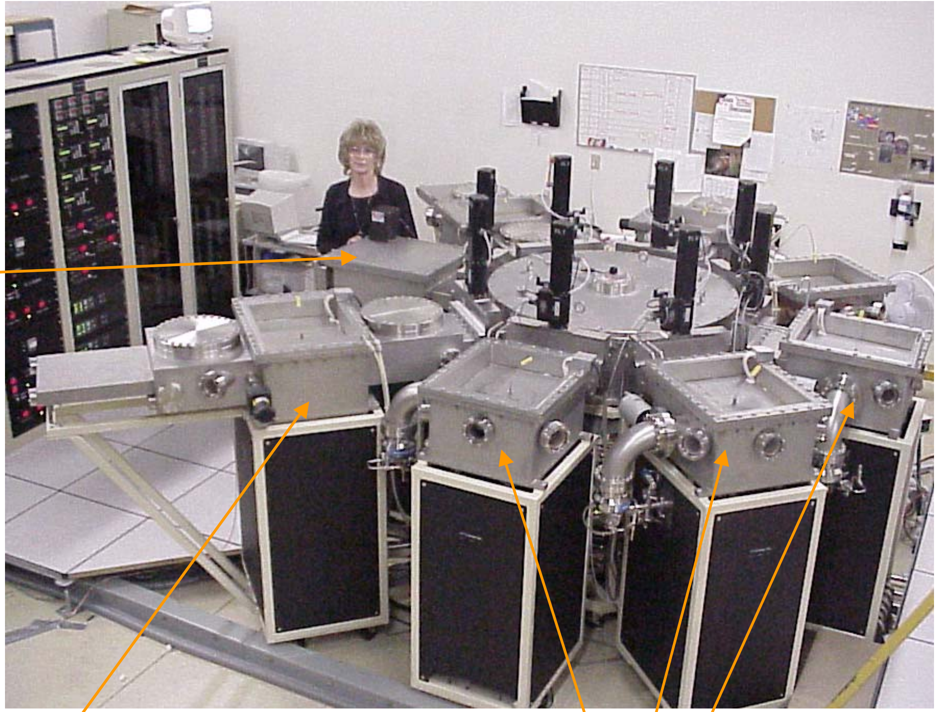
** σ_L and σ_d – Photo- and dark conductivity.*
*** γ is derived from $\sigma_L \propto \mathbf{F}^{\gamma}$, where F is the intensity of illumination (equivalently generation rate). For good intrinsic i layer with low density of states: $0.9<\gamma<1$.*

Progress: Work Performed since 2008 Annual Merit Review and Peer Evaluation Report

- Fabrication of an integrated hybrid PEC device containing a-Si tandem solar cell and a-SiC photoelectrode.
- Investigation of the effect of surface oxide (SiOx) on the photocurrent
- Improvement of the PV performance of a-Si tandem solar cell used in the hybrid PEC device

Progress: Deposition of a-SiC Material and Photoelectrode

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.

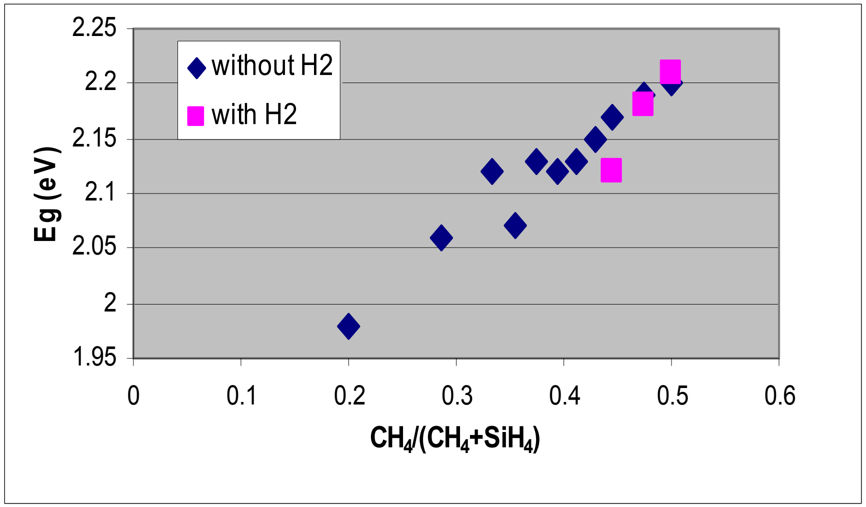


Main deposition parameters:

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**

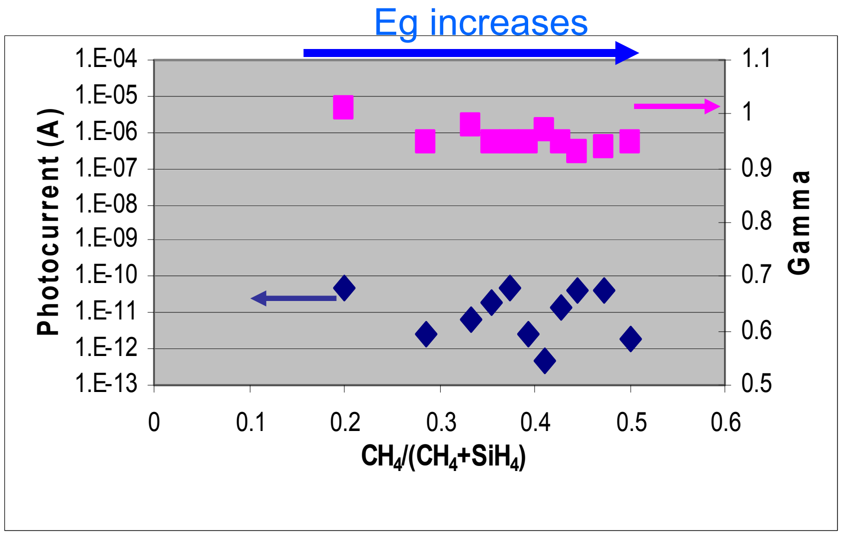
Progress: Opto-electronic Properties of a-SiC

E_g vs. $CH_4/(CH_4+SiH_4)$



- Thickness of a-SiC films: 400-450 nm
- Dark conductivity $\sigma_d < 10^{-10}$ S/cm
- H_2 concentration in a-SiC 7~9%

Normalized I_{ph} & γ vs. $CH_4/(CH_4+SiH_4)$



- The measured photocurrent is normalized at 550 nm using the following equation:

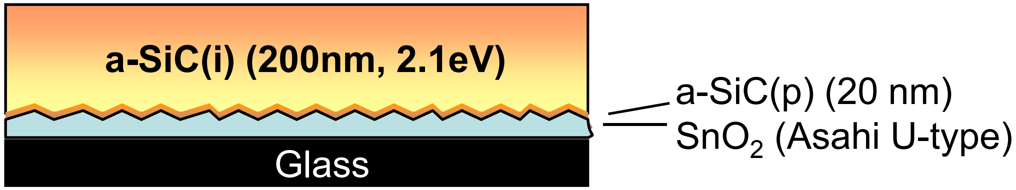
  $I_{ph} = e.N_{ph}(\lambda)\,[1-R(\lambda)].[1-\exp(-\alpha(\lambda)d)].\eta\tilde{\imath}/\tau$

- γ is derived from $I_{ph} \propto F^{\gamma}$, indicative of density of states (DOS) in the film. For good intrinsic i layer with low DOS: $0.9<\gamma<1$.

At a bandgap of ~2.2 eV, the a-SiC films have good optoelectronic properties

Progress: PEC Characteristic of a-SiC Photoelectrode

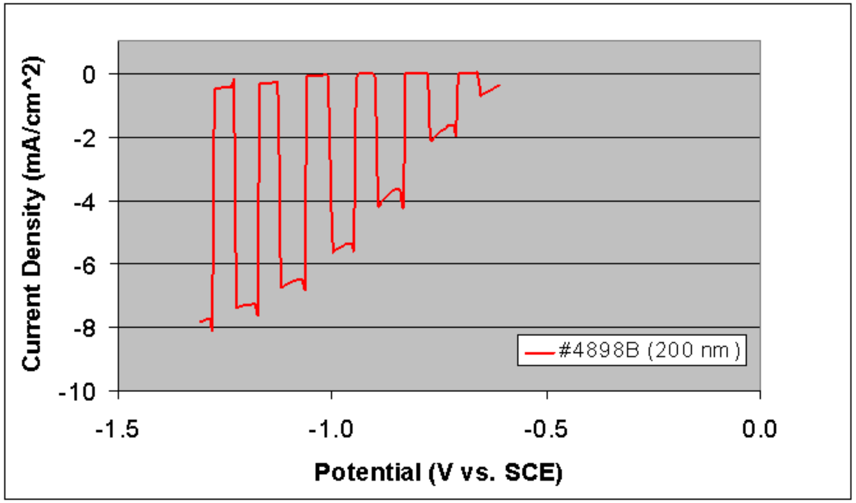
Configuration



Main features:

- Behaves like a p-type photoelectrode
- Photocurrent: 7-8 mA/cm2 (tested in 3-electrode setup)
- Flatband voltage: +0.26V (vs Ag/AgCl)
- Durability: up to 100 hrs in pH2 electrolyte (so far tested)

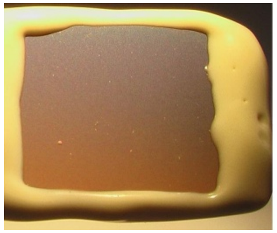
Photocurrent vs. potential



*In 0.5M H_2SO_4 electrolyte. [Data measured by HNEI]

Surface Morphology

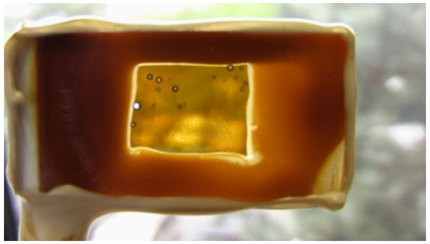
Before testing



On SnO_2 substrate

After 24-hr PEC test

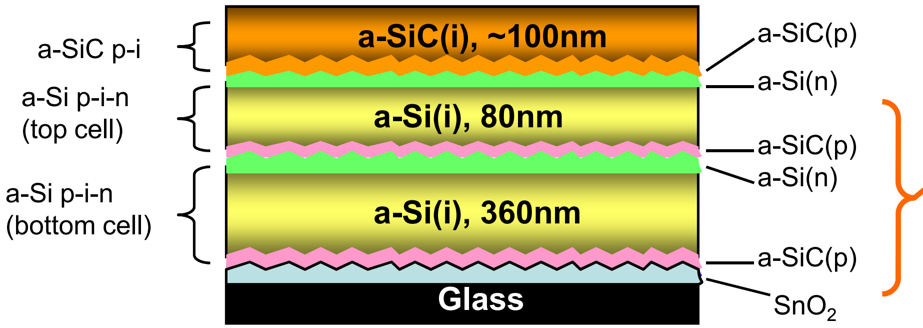
After 100 hrs PEC test



[Data measured by NREL]

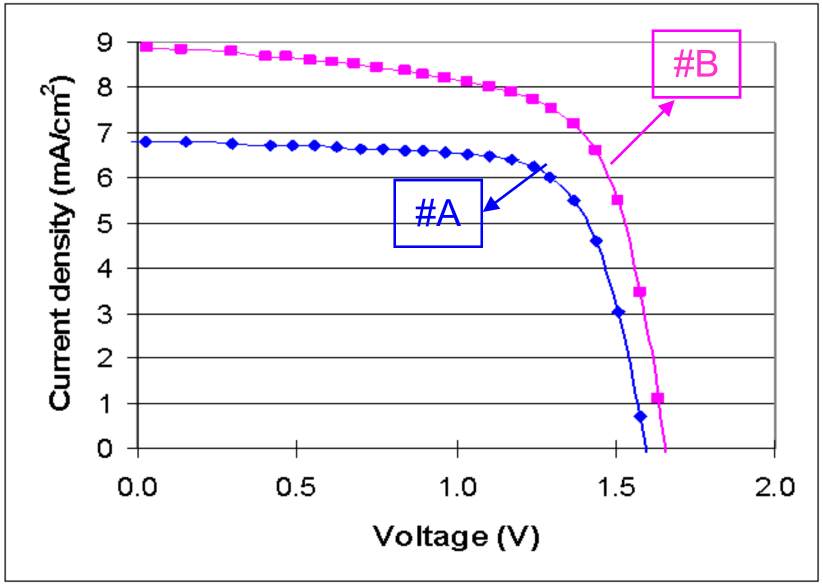
Progress: Performance of a-Si Tandem Device

Configuration of a hybrid PEC cell



A-Si tandem solar cell --- major component in the hybrid PEC cell

Current vs. Voltage

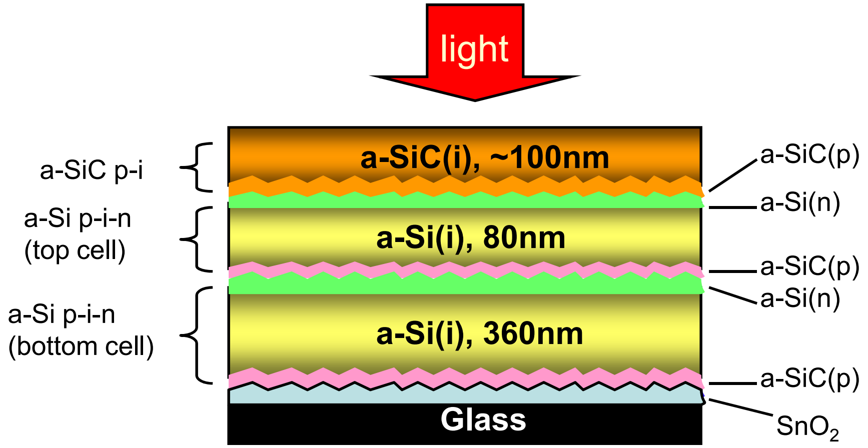


Comparison of PV performance

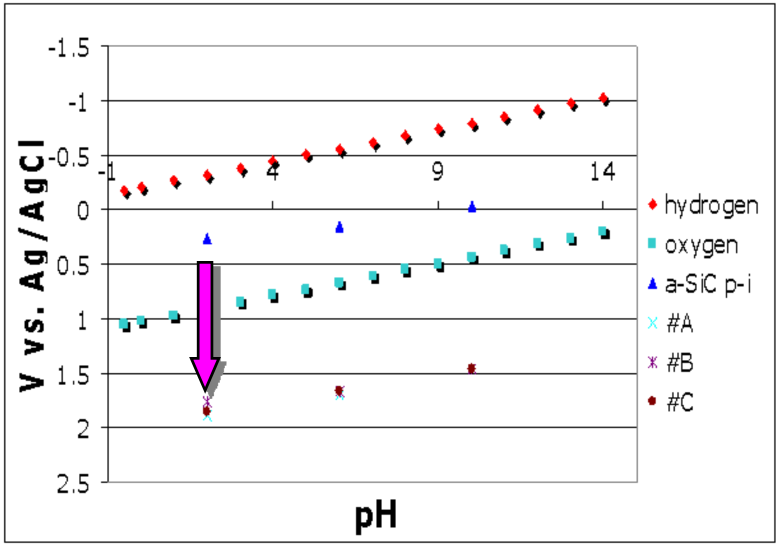
SN	Jsc (mA/cm^2)	Voc (V)	FF	Eff. (%)
#A	6.795	1.6	0.717	7.79
#B	8.70	1.66	0.67	9.62

- #A -used in the first hybrid PEC cell.
- #B- improved device. Shall incorporate into the hybrid PEC device.

Progress: Hybrid PEC Cell: Flatband Voltage (V_{fb})



Flatband voltage vs. pH



•#A, #B and #C - hybrid PEC devices.

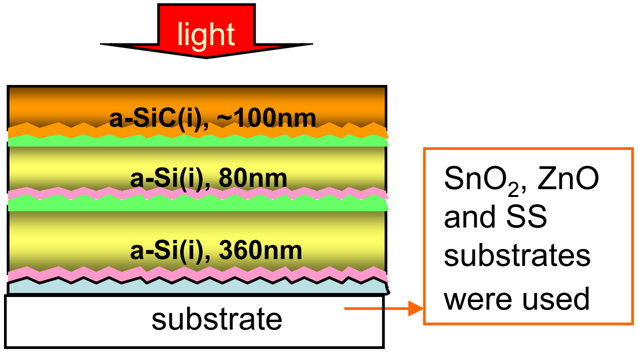
- V_{fb} determined by the illuminated open-circuit voltage (IOCP).
- For the p-type photoelectrode, V_{fb} needs to be below H_2O/O_2 redox potential for water splitting.
- In the hybrid PEC device, the flatband voltage shifts by ~+1.6V or +0.97V below H_2O/O_2 potential at pH2

[Data measured by NREL]

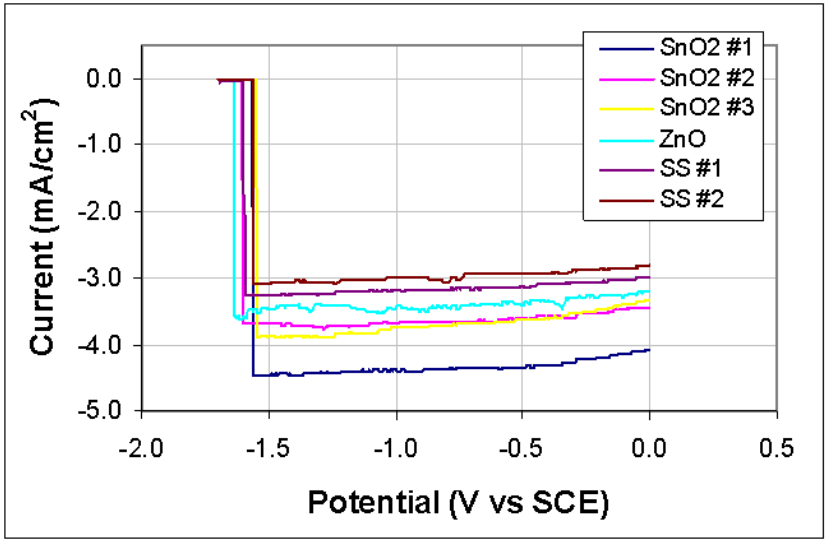
<u>Progress</u>: Hybrid PEC Cell: Photocurrent

Test conditions:

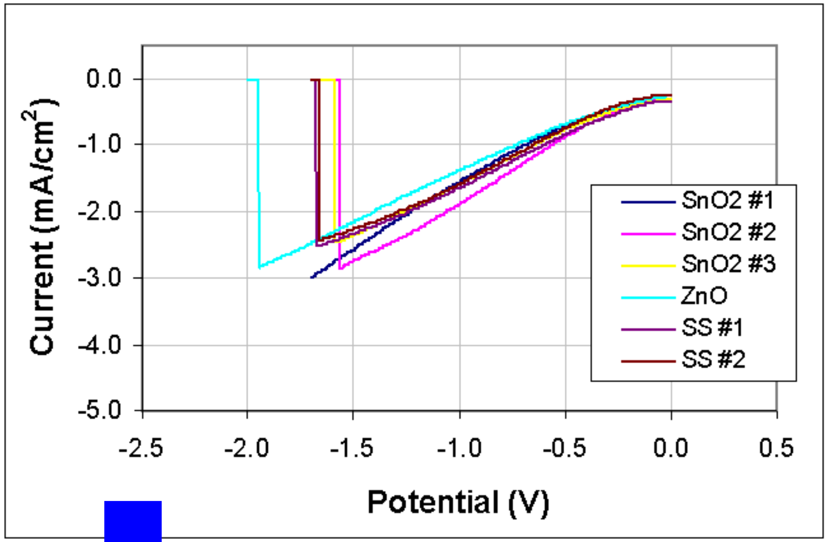
- **Sample tested:** *hybrid PEC cell*
- **Counter electrode:** *Pt*
- **Electrolyte:** *buffer pH2 (*sulphamic acid solution with added potassium biphthalate)



Current vs. potential (3-electrode)



Current vs. potential (2-electrode)



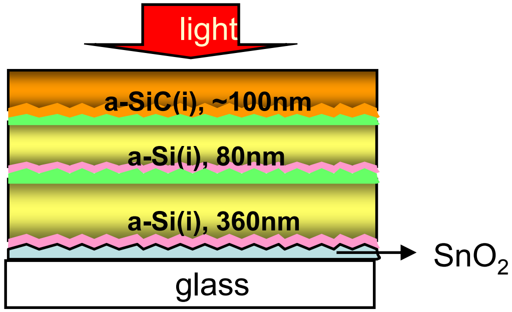
[Data measured by HNEI]

Photocurrent at zero bias is much smaller than in the 3-electrode set up, suggesting existence of limiting factors such as, type of ***electrolyte***, ***counter electrode*** and formation of ***SiOx*** on the surface.

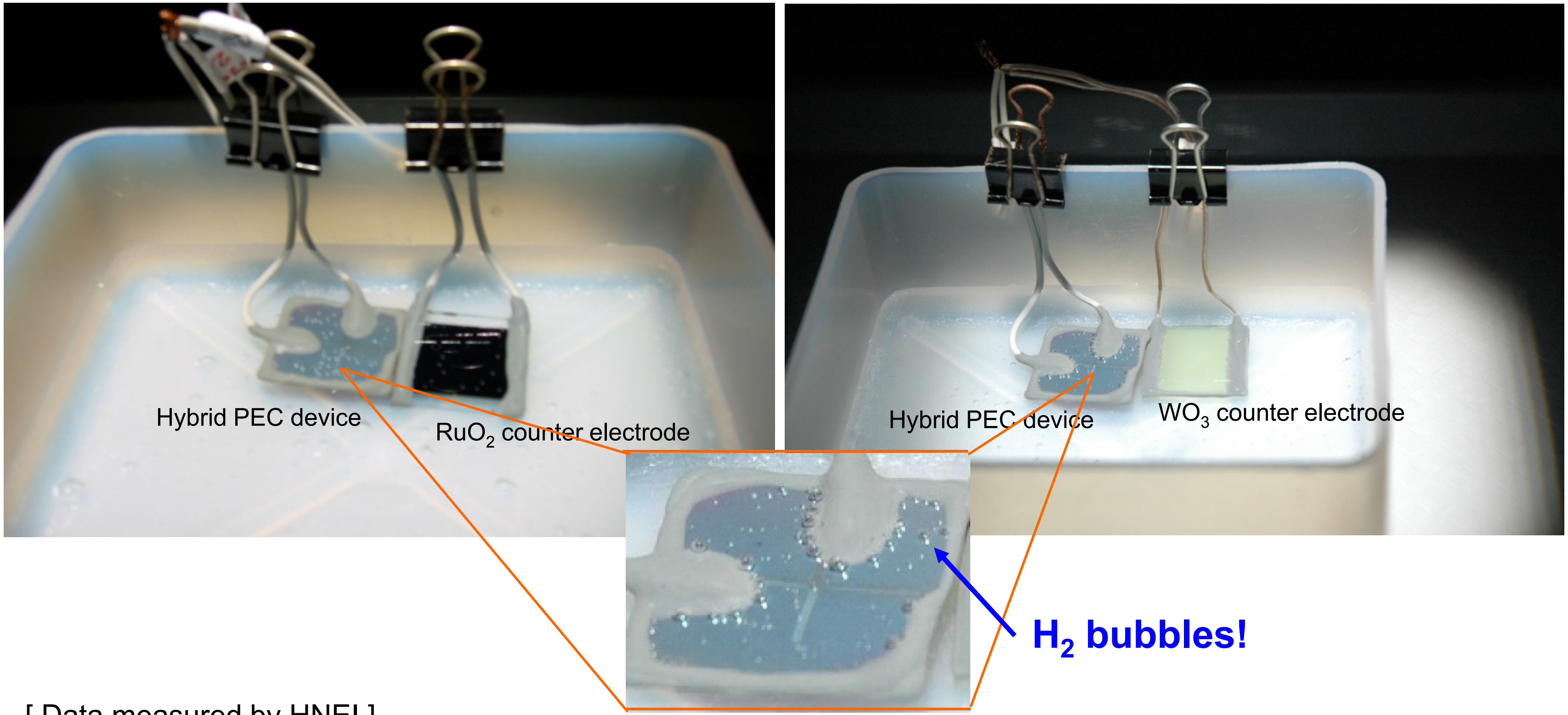
Progress: Hydrogen Evolution

Test conditions:

- **Sample tested:** *hybrid PV/PEC cell*
- **Counter electrode:** *RuO_2 or WO_3*
- **Electrolyte:** *0.33M H_3PO_4*



With RuO_2 counter electrode **With WO_3 counter electrode**

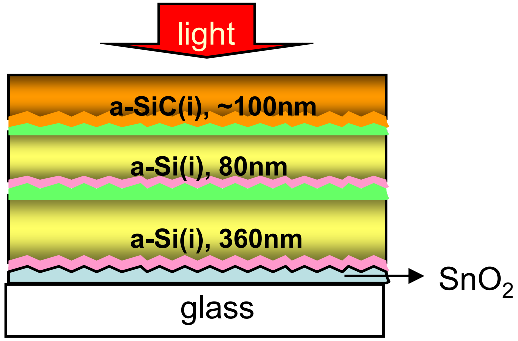


[Data measured by HNEI]

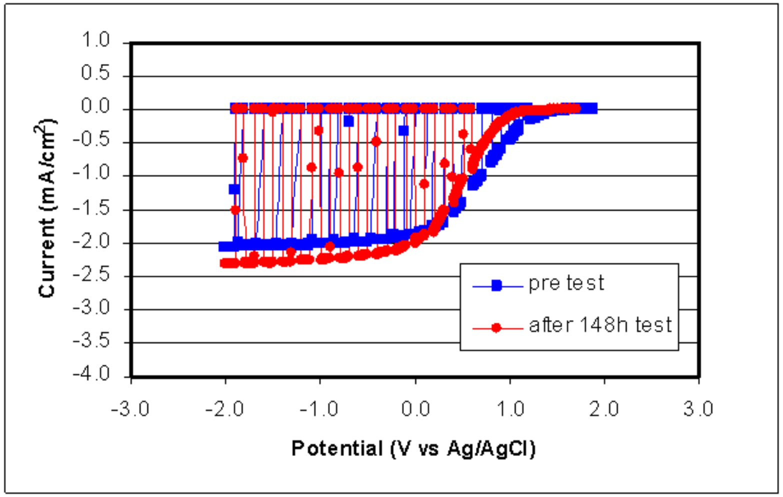
Progress: Corrosion resistance up to ~150 hrs

Test conditions:

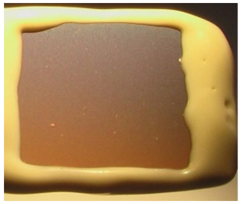
- **Sample tested:** *hybrid PEC cell*
- **Counter electrode:** *Pt*
- **Electrolyte:** *buffer pH2*
- **Current bias:** *1.6 mA/cm²*



Current vs. potential (before and after test)



Before testing



On SnO_2 substrate

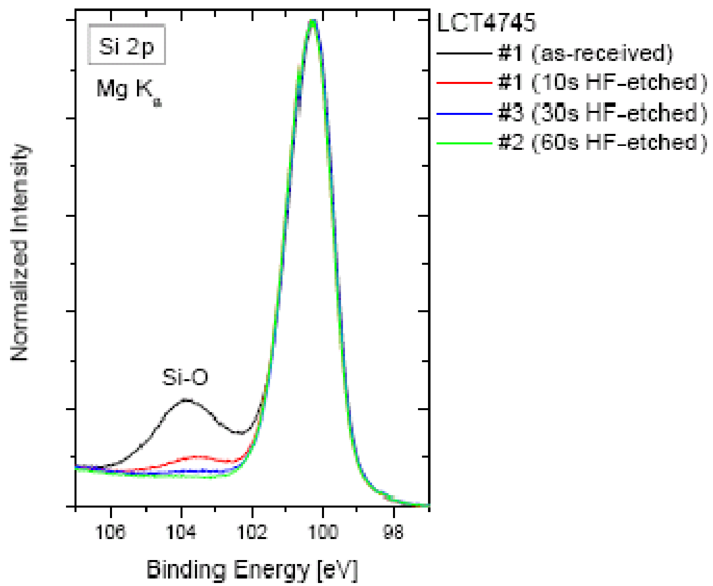
After 148 hrs testing

- H_2 production throughout the test
- Little degradation after corrosion test for 148 hrs

[Data measured by NREL]

Progress: Surface Treatment by HF Acid

XPS spectra on a-SiC films

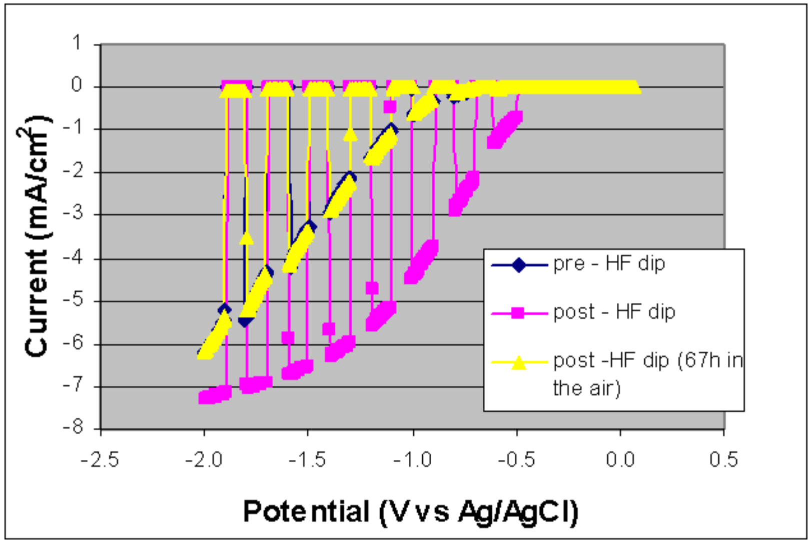


* HF (hydrofloric acid) concentration = 48%

[Data measured by UNLV]

- A few nm thick SiOx formation on a-SiC surface
- After HF etch for 30-60s, SiOx layer removed

Effects of SiOx on photocurrent



* 24% HF for 30 sec.

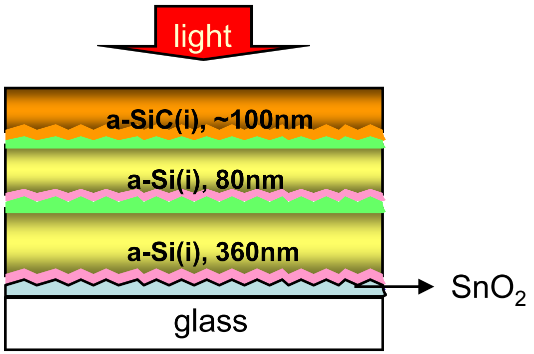
[Data measured by NREL]

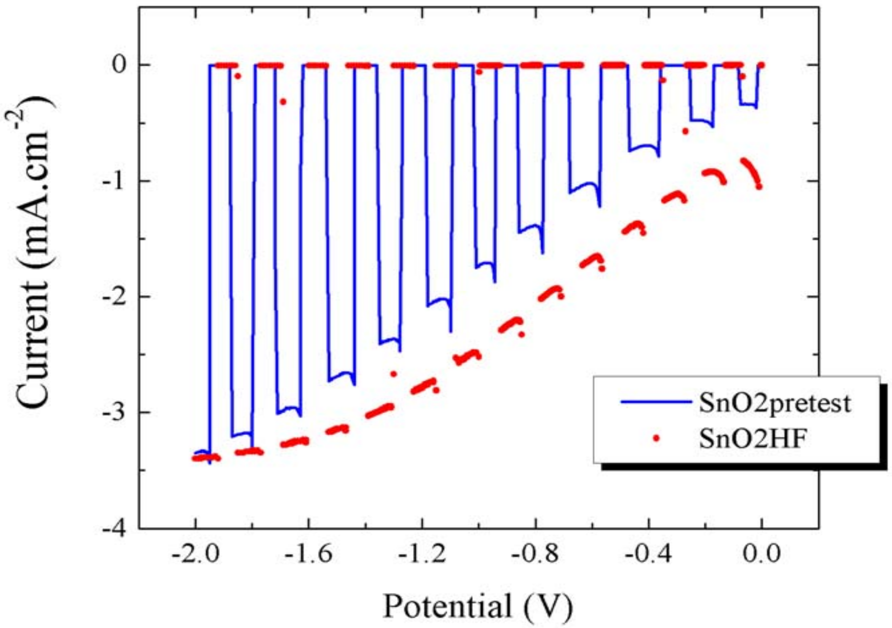
- After HF etch for 30s, photocurrent increases and its onset shift anodically
- Photocurrent degrades and reverts to its initial value when the a-SiC photoelectrode is exposed to the air

Progress: Effect of HF Etch on Photocurrent of the Hybrid PEC Device

Test conditions:

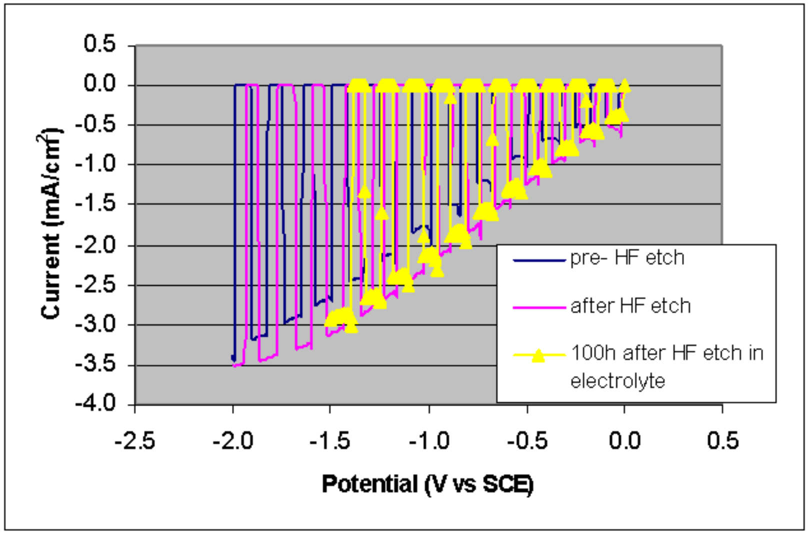
- **Sample tested:** *hybrid PEC cell*
- **Electrolyte:** *buffer pH2*
- **Counter electrode:** *RuO_2*
- **HF dip:** *5% HF for 30 sec*





Photocurrent increases after HF etch:
0.33 → 0.83 mA/cm² @0V.

After HF etch, photocurrent of the hybrid PEC device changes little in electrolyte for up to 100 hrs



[Data measured by HNEI]

Collaborations

- Partners:
  - Hawaii Natural Energy Institute (Academic): collaboration about characterization of new photoelectrode materials and the hybrid PEC device;
  - National Renewable Energy Laboratory (Federal): collaboration to perform durability tests on new photoelectrode materials, hybrid PEC device and surface modification;
  - University of Nevada at Las Vegas (Academic): collaboration to analyze the surface energy band structure of new photoelectrode materials.

Future Work

- Improvement of photocurrent in the hybrid PEC cell.

  Focus – minimize over-potential losses to enhance the photocurrent at zero potential using 2-electrode setup.

1. Modify the surface structure of intrinsic a-SiC using the following approaches,
   a. thin SiNx layer deposition on the a-SiC photoanode.
   b. C-rich surface for minimizing the formation of SiOx. This can be controlled via altering the deposition conditions during growth of the a-SiC film.
   c. deposition of a thin halogenated layer on a-SiC photoanode.
   d. Use Pt nano-particles for surface modification.

2. Analyze the surface structure of the a-SiC photoelectrode after a 100-hour test, in order to understand why the photocurrent of the a-SiC photoelectrode increased while its onset shifted anodically after a 100 hr durability test. This work will be collaborated with UNLV group.

3. Improve the counter electrode.
   - Explore other counter electrode materials (under evaluation).

Future Work *(cont'd)*

- Improvement of photocurrent in the hybrid PEC cells.

<u>Objective:</u> Fabricate the a-Si tandem solar cell to with efficiency > 10%, by

(a) minimizing the damage induced by the sputtering (growth of ZnO or ITO) process;
(b) using a lower bandgap intrinsic material in the bottom cell to enhance Jsc.

Simultaneously use stainless steel (SS) to replace glass/SnO_2 as the substrate and fabricate a-Si tandem device on it. With improved a-Si tandem device, fabricate hybrid PEC devices to increase the solar-to-hydrogen efficiency.

- Durability tests.
  - Extend the durability test of a-SiC photoelectrodes to 200-hour.
  - Improve the durability using Pt nano-particles

- Development of the a-SiNx photoelectrode.
  - High photosensitivity ($\sigma_L/\sigma_d = 10^5$-10^6) achieved, with Eg ~ 2 eV
  - Solar cells using a-SiNx as the absorber layer: under going.
  - The a-SiNx photoelectrode: fabricated and being tested.

Amorphous Silicon Carbide Summary

- Hydrogen evolution (bubbles) was successfully demonstrated in the hybrid a-Si tandem solar cell/a-SiC photoelectrode (PEC) cell.

- The hybrid PEC cell, fabricated using the PECVD technique, exhibits following characteristics:
  - Flatband voltage: shifts by ~+1.6V
  - Photocurrent: 3-5 mA/cm^2 (3-electrode); ~0.83 mA/cm^2 (@0V) (2-electrode)
  - Photocurrent measured in 2-electrode setup is affected by
    ------ type of electrolyte;
    ------ type of counter electrode;
    ------ thin SiOx on the surface of a-SiC.

- The hybrid PEC cell exhibits excellent durability in pH2 electrolyte for up to ~150 hrs (so far tested).

- PV performance of a-Si tandem solar cells has been improved:

Device Configuration	Jsc (mA/cm2)	Voc (V)	FF	η (%)
SnO_2/pin/pin/ZnO/Ag	8.70	1.656	0.668	9.62
SnO_2/Ag/ZnO/a-Si pin/pin/ITO	8.58	1.694	0.682	9.91

Project Summary

➢Relevancy

The MVSystems/UH project is accelerating the development of **three important PEC thin-film materials classes** (a-SiC, WO3 and CGSe) with high potential for reaching DOE goals of practical PEC water-splitting.

➢Approach

Use existing knowledge of the three PEC thin-film materials and their PV performances to apply them to a PEC system for hydrogen production.

➢Progress

Items	Thin-film materials	2008			2009			Note
		Target	Achieved	Status	Target	Achieved	Status	
Material photocurrent	a-SiC	≥ 3 mA/cm^2	7-8 mA/cm^2	100%	≥ 4 mA/cm^2	7-8 mA/cm^2	100%	
	WO_3		2.8-3 mA/cm^2	100%		3.6 mA/cm^2	90%	
	CGSe		20 mA/cm^2	100%		20 mA/cm^2	100%	
Material/Device durability	a-SiC	≥ 100 hrs	100 hrs	100%	≥ 200 hrs	150 hrs	75%	
	WO_3		100 hrs	100%		100 hrs	50%	
	CGSe		10 hrs	10%		10 hrs	5%	
Device STH efficiency	a-Si/a-SiC				≥ 5%	1%	25%	H_2 production observed
	WO_3					3.2%	65%	expected from current matching
	CGSe							

Project Summary (Cont'd)

- Collaboration

In order to promote the needed scientific breakthroughs in PEC R&D, collaborations have been developed within the US DOE PEC Working Group and with the IEA-HIA PEC Annex-26.

- Future work

(1) Further improve the properties of thin-film materials.
(2) Develop new surface modification techniques.
(3) Establish band diagrams for the thin-film photoelectrode/electrolyte system.
(4) New techniques will be used to evaluate PEC films interface @ UNLV and use new information to focus fabrication and device matching efforts effectively.
(5) Improve the PV performance of the thin-film solar cell used in the hybrid PEC device.