PD053

PHOTOELECTROCHEMICAL HYDROGEN PRODUCTION

Arun Madan

MVSystems, Inc.

June 7, 2010

Project ID # DE-FC36-07GO17105

Overview

Timeline

- Project start date: 9/1/2007
- Project end date: 12/31/2010
- Percent complete: ~75%

Budget

- Total project funding*
  - DOE share: $**1,508,827**
  - Contractor share: $**415,128**

** funds cover work reported in posters PD053, PD054, and PD055*

Barriers

- Challenges for photoelectrochemical hydrogen production technologies:

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

Partners

Hawaii Natural Energy Institute (HNEI)

National Renewable Energy Laboratory (NREL)

- <u>Collaborators:</u>
  University of Nevada at Las Vegas (UNLV)
  Stanford University (Academic)
- <u>Project Lead:</u> MVSystems, Inc.

Overview

poster #PD053
Progress in the Study of ***Amorphous Silicon Carbide*** as a Photoelectrode in Photoelectrochemical Cells

poster #PD054
Progress in the Study of ***Tungsten Oxide Compounds*** as Photoelectrodes in Photoelectrochemical Cells

poster #PD055
Progress in the Study of ***Copper Chalcopyrites*** as Photoelectrodes in Photoelectrochemical Cells

Poster #PD053

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

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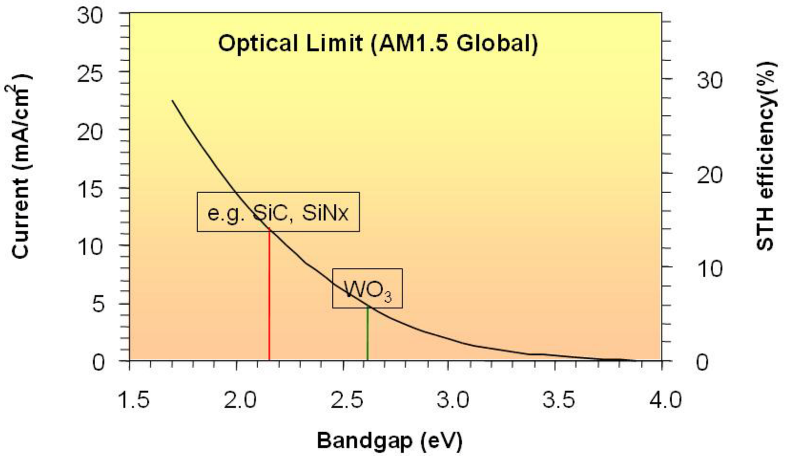
Relevance – Objectives

Advantages of a-SiC photoelectrode:

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

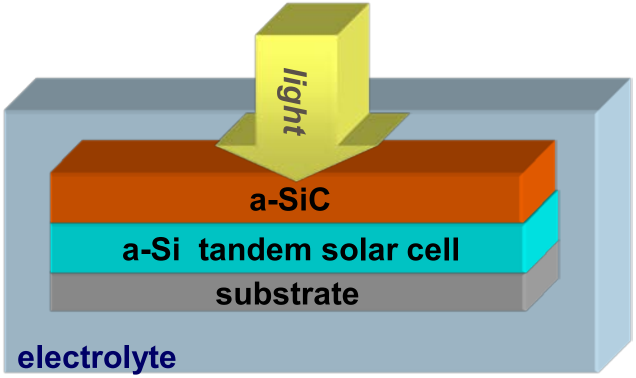


Maximum current available vs. material bandgap (Eg).

Our goal …

By December 2010, fabricate a hybrid a-Si tandem solar cell / a-SiC photoelectrode (PV/a-SiC) device which exhibits*:

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



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

** Original goal from "Statement of Project Objective", DE-FG36-07GO17105, Attachment #5.*
This requirement has been postponed until the end of 2010.

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 hours	100% @ 6/2008	
Year 2: (10/2008----9/2009)		
✓ Material photocurrent ≥ 4 mA/cm^2	100% @ 1/2008	7-8 mA/cm^2 demonstrated with a-SiC-based PEC electrode
✓ Durability: 200 hours	75% @ 2/2009	durability of 150 hours achieved.
✓ Device STH efficiency ≥ 5%	20% @ 11/2008	1% efficiency achieved with hybrid device (~ 0.83 mA/cm^2).
Extended Year : (9/2009----12/2010)		
✓ Durability: 200 hours	100% @ 1/2010	durability of 200 hours achieved.
✓ Device STH efficiency ≥ 5%	30% @ 9/2009	1.6% efficiency achieved with hybrid device (~ 1.26 mA/cm^2).

Relevance – Barriers

Barrier	Challenges	Strengths
Y. Materials Efficiency	Currently the band-edge of a-SiC appears to be poorly aligned for water splitting	– Hybrid devices are able to produce > 5mA/cm^2 (in solid-state version). Surface modification of a-SiC will unlock this potential and lead to water splitting devices with efficiency exceeding 6%. – Bandgap may be readily tuned from 2.0 to 2.3 eV. – Flatband voltage shifts +1.6 V when photoelectrodes are integrated with a-Si tandem PV cells to allow unassisted hydrogen generation.
Z. Materials Durability	Photocorrosion over extended time periods in conductive electrolytes	– Stability up to 200 hours in pH2 electrolyte demonstrated. – Corrosion is localized, i.e. it begins at occasional defects, not due to bulk material vulnerability
AC. Device Configuration Designs	Tandem thin-film-silicon solar cells need to be improved to maintain adequate current and voltage while the incident light is filtered by the a-SiC photoelectrode	– Comprehensive modeling shows the hybrid PEC cell has the potential of achieving 10% solar-to-hydrogen (STH) efficiency. – Same technology is used to fabricate the photoelectrode as well as the tandem PV cell, so the two are readily integrated in the same deposition system. – Nearly 2% STH efficiency demonstrated.

Approaches

From 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 (infrared spectroscopy)**
- **Device performance (p-i-n solar cells)**

a-SiC photoelectrode

- **Photocurrent**
- **Flatband voltage**
- **Durability in electrolyte**
- **Surface modification**
- **Surface band alignment**

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 $\boldsymbol{\sigma_L} \propto \mathbf{F}^{\gamma}$, where F is the intensity of illumination (equivalently generation rate). For good intrinsic i layer with low density of states: $0.9<\gamma<1$.*

Additional materials evaluation: nc-SiC, a-SiCN, nc-SiNx, a-SiON

Work Performed since 2009 Annual Merit Review and Peer Evaluation Report

- Improvement of the PEC performance of the integrated hybrid PV/a-SiC device (containing a-Si tandem solar cell and a-SiC photoelectrode)

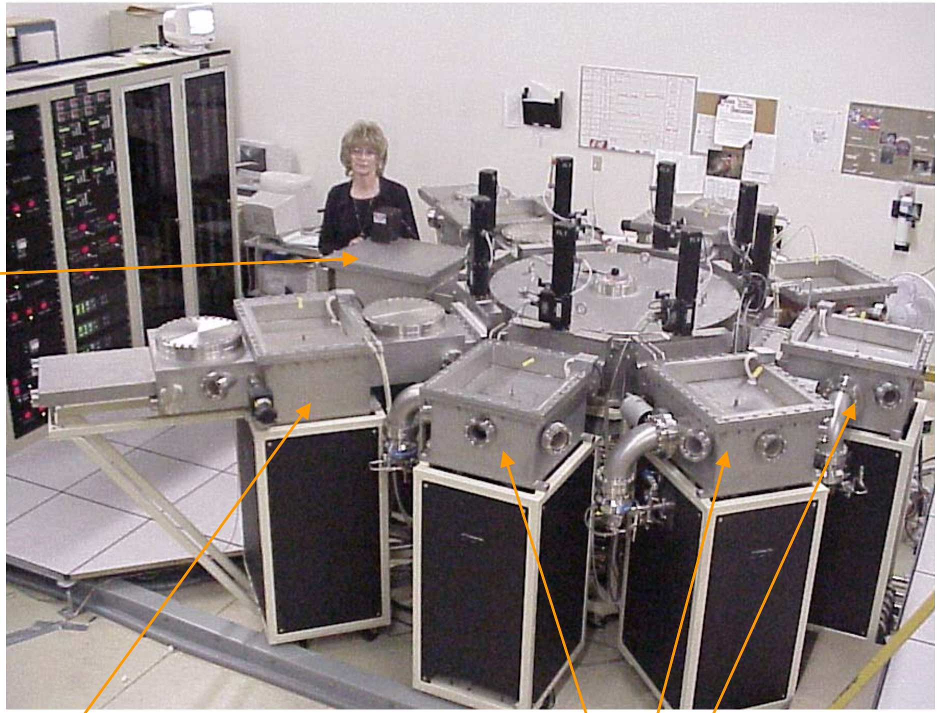
- Durability improvement

- Investigation of the effect of surface modification on the photocurrent using various methods

- Improvement of the PV performance of a-Si tandem solar cell used in the hybrid PEC device

<u>Progress</u>: 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.

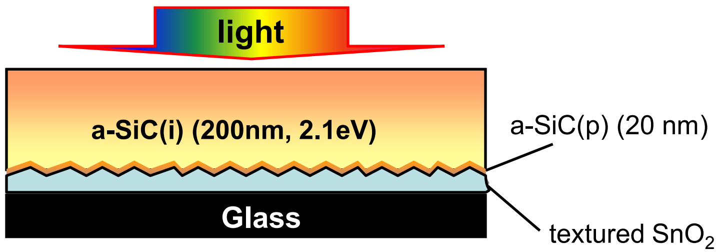


Main deposition parameters:

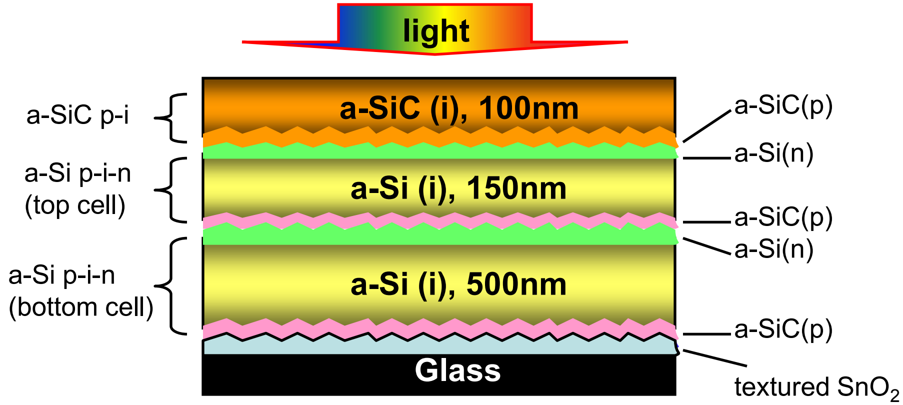
RF power:	**10-20 W**
Excitation frequency:	**13.56 MHz**
Pressure:	**300-550 mTorr**
SiH_4 flow rate:	**20 sccm**
CH_4 flow rate:	**0-20 sccm**
H_2 flow rate:	**0-100 sccm**
Substrate temperature:	**200° C**

http://www.mvsystemsinc.com

Progress: PEC Characteristics of a-SiC Photoelectrode and integration with a tandem PV cell



a-SiC p/i photoelectrode



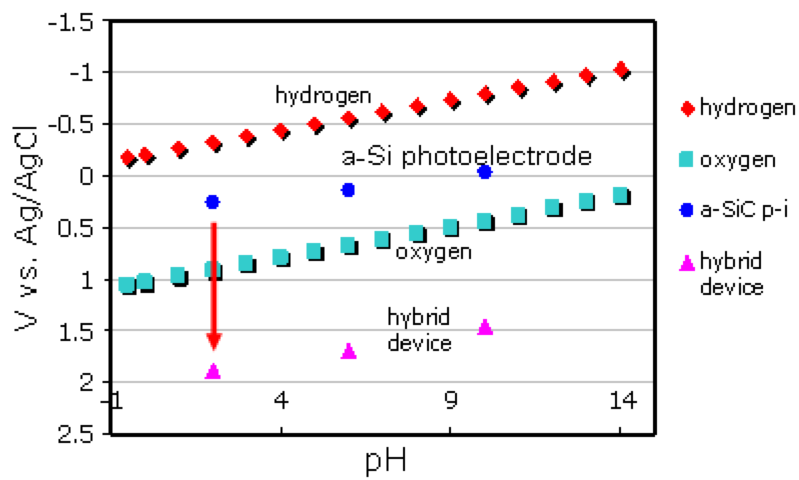
Thin-film-silicon PEC hybrid device

Main Features of a-SiC p/i Photoelectrode:

- Behaves like a p-type photoelectrode
- Saturated photocurrent: up to 8 mA/cm^2
- Flatband voltage: +0.26V (vs Ag/AgCl)

◆ The flatband voltage of the a-SiC p/i photoelectrode is above the water oxidation half-reaction potential which means external voltage is required to initiate water splitting.

◆ Integration with tandem a-Si solar cells shifts the flatband voltage of the system to 1.5 - 2.0 Volt region where hydrogen generation is possible.



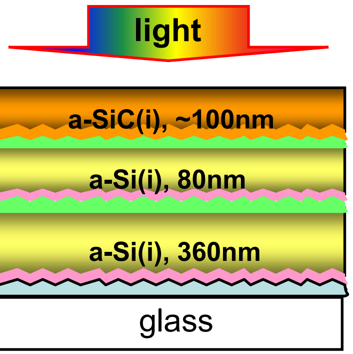
Flatband voltage V_{fb} vs. pH for an a-SiC p/i photoelectrode and a hybrid PEC device

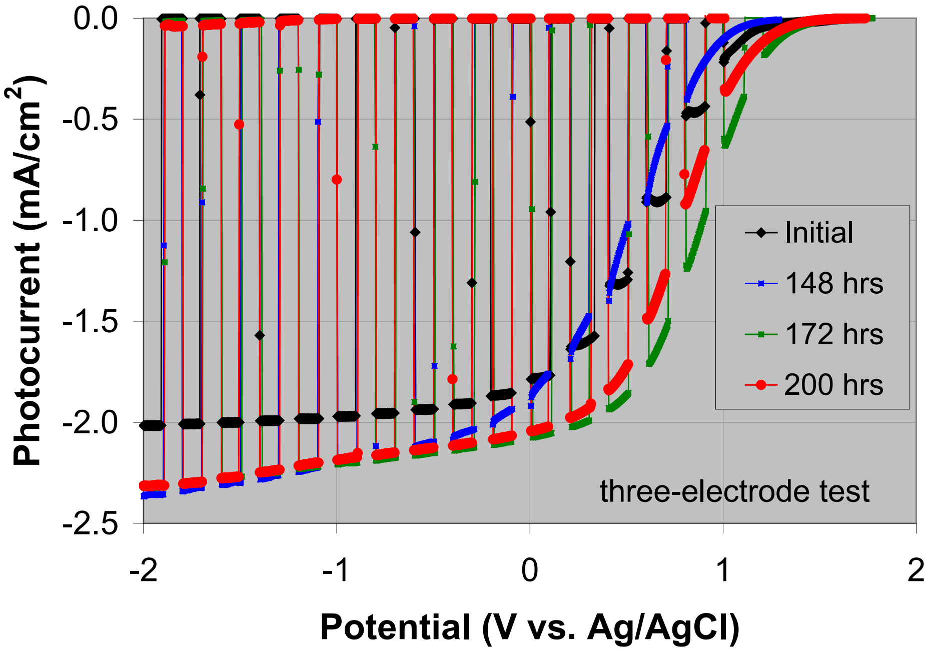
[Data measured by NREL and HNEI]

<u>Progress</u>: 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)

Before testing

After 200-hr testing

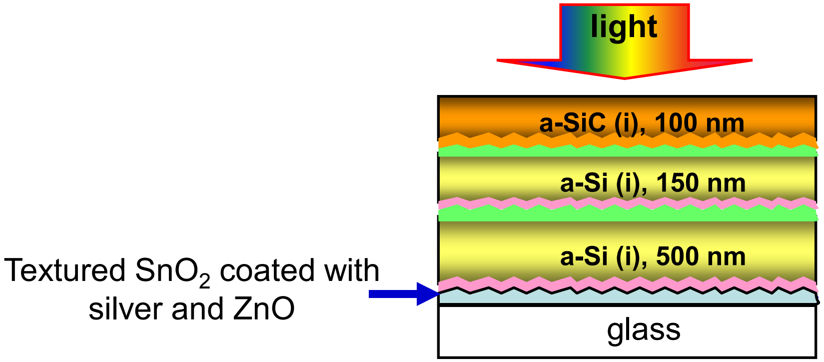
- H_2 production throughout the test
- No degradation during durability/corrosion test for 200 hours (So far)

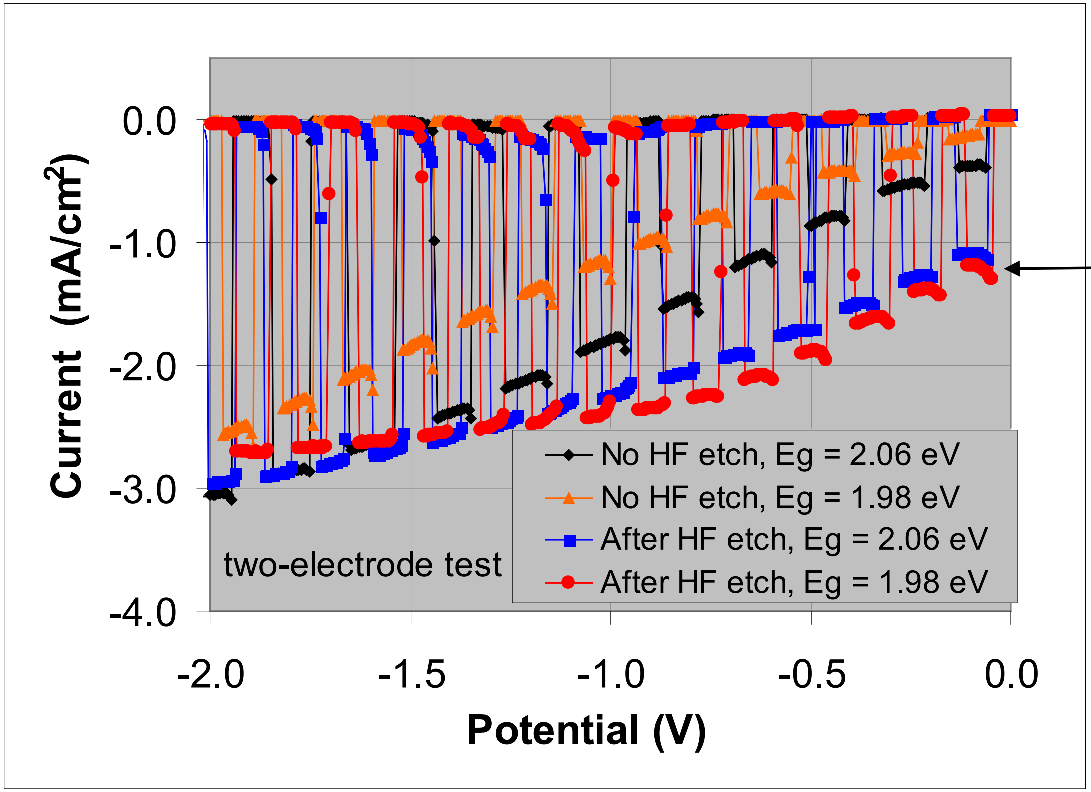
[Data measured by NREL]

Progress: Current and STH Efficiency

Test conditions:

- **Sample tested:** *hybrid PEC cell with ZnO/Ag back reflector*
- **Setup:** *2-Electrode*
- **Counter electrode:** *RuO_2*
- **Electrolyte:** *buffer pH2*



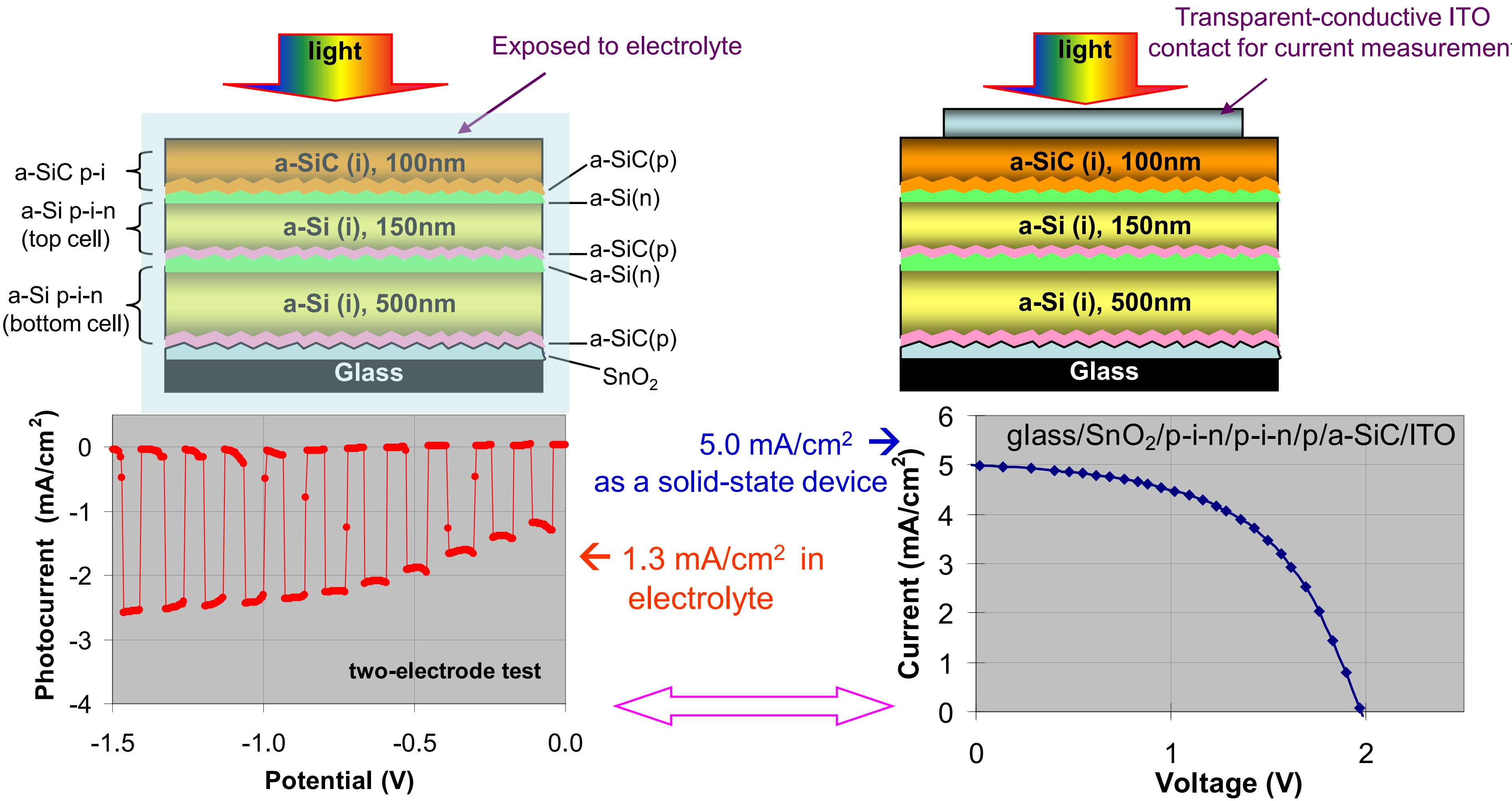


1.3 mA/cm² achieved by removal of silicon oxide from a-SiC with HF etch.

This current density corresponds to 1.6% solar-to-hydrogen (STH) efficiency

[Data measured by HNEI]

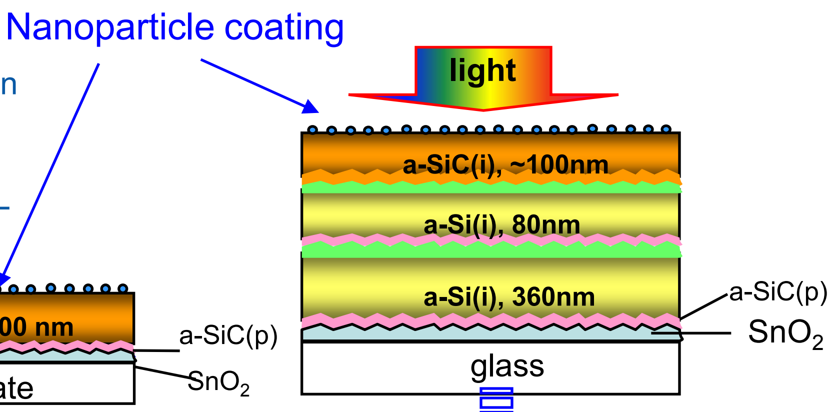
<u>Progress</u>: Comparison with a Solid-State Configuration

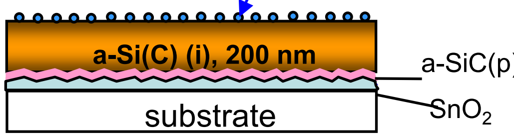


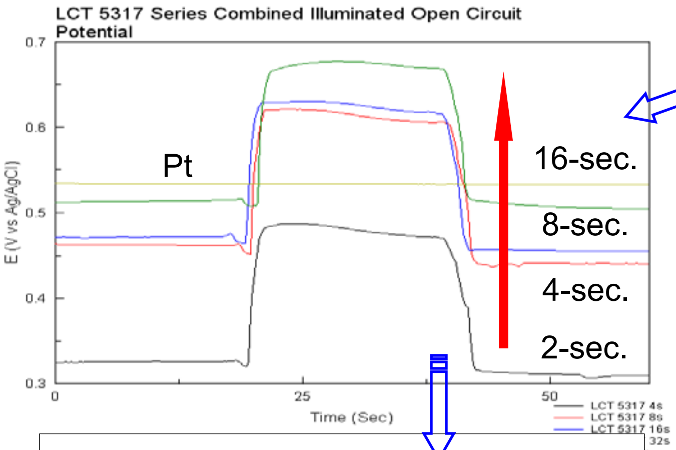
- ➢STH efficiency of hybrid PEC cell should be >6% base on solid state version (right)
- ➢Low current in hybrid PEC cell (left)
- ➢<u>Charge carrier extraction problem at the a-SiC/electrolyte interface</u>

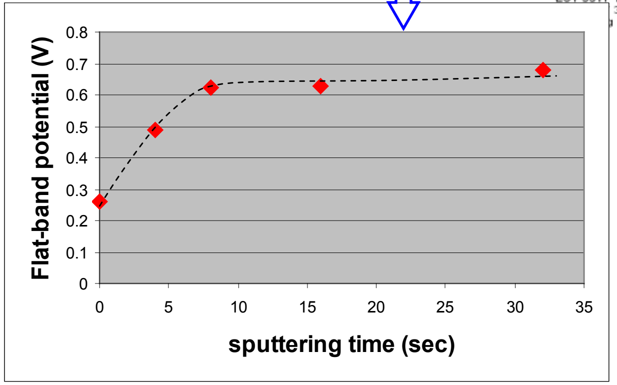
Progress: Surface modification – use of nanoparticles (Pt/Au)

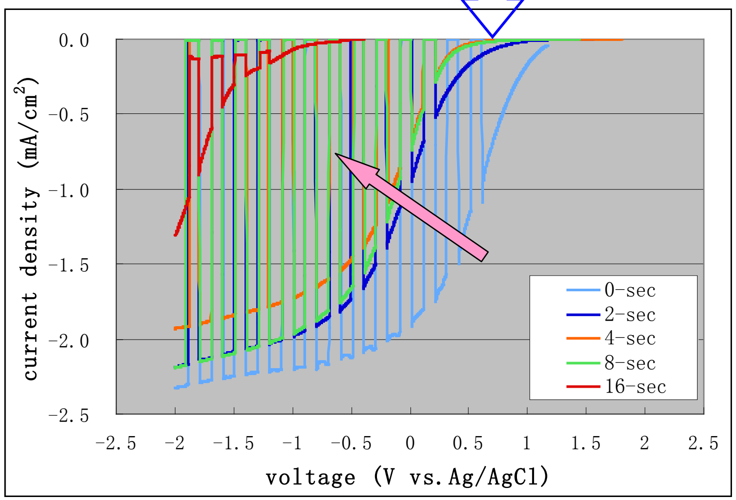
- Purpose: To determine the effect of time-dependent Pt/Au sputtering on PEC performance of a-SiC samples.
- Pt/Au was fabricated by sputtering in Dr.YanFa Yan's group at NREL
- PEC characteristic was measured by Dr.Todd Deutsch's group at NREL









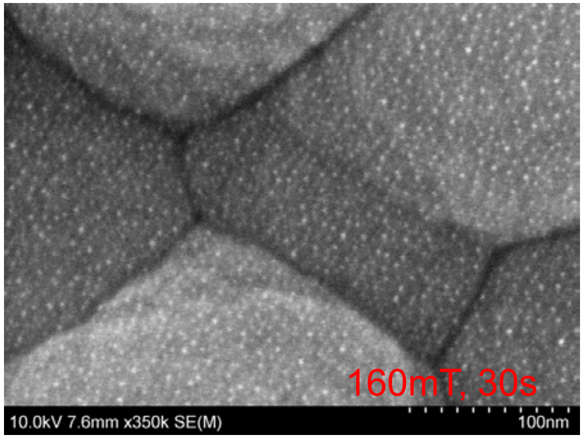


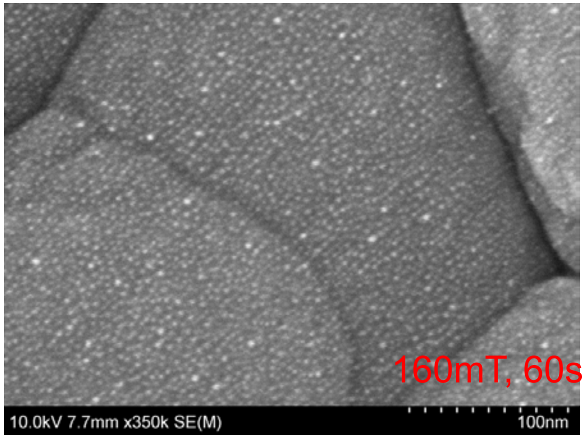
- All samples had more negative photocurrent onset potential than pure Pt electrode
- Increase of hydrogen evolution reaction overpotential with increasing sputtering time
- A barrier at the Pt/Au / a-SiC interface is most likely formed.

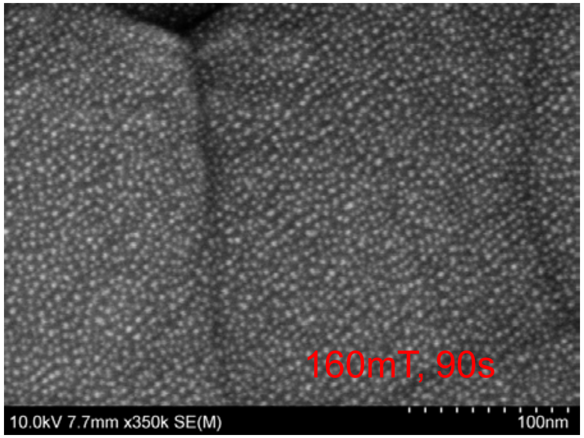
Progress: Surface modification – use of nanoparticles (Pd/Au)

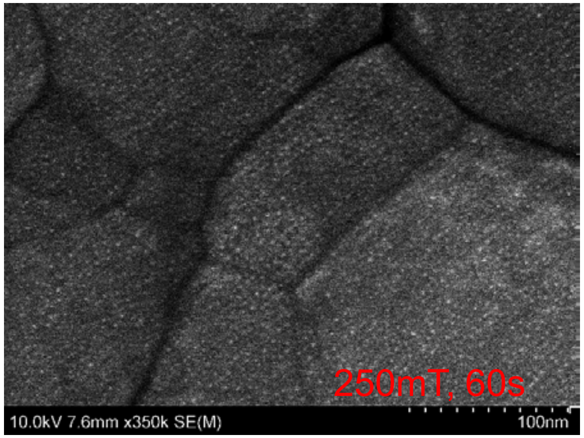
• Pd/Au nano-particles were deposited using a "metalizer" (sputtering system) commonly used to coat non-conductive samples before SEM analysis.
• Before nano-particles deposition, a-SiC were immersed in 5%HF to remove the SiOx layer.
• Deposition parameters include time and pressure (160mT or 250mT). All depositions were done at a constant current of 15mA.

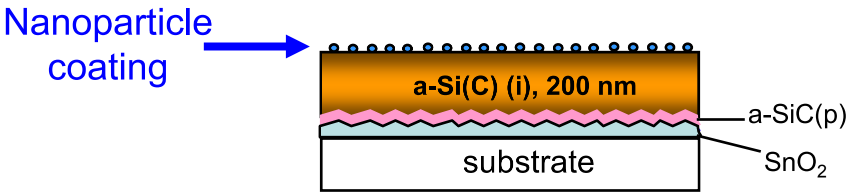
SEM images of Pd/Au nano particles on a-SiC surface









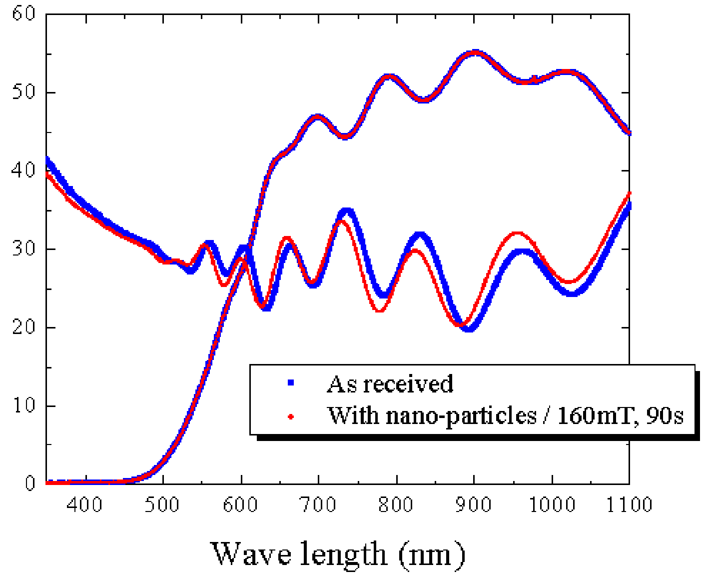


Nano-particles size is approx. 2-4 nm Size & density can be controlled

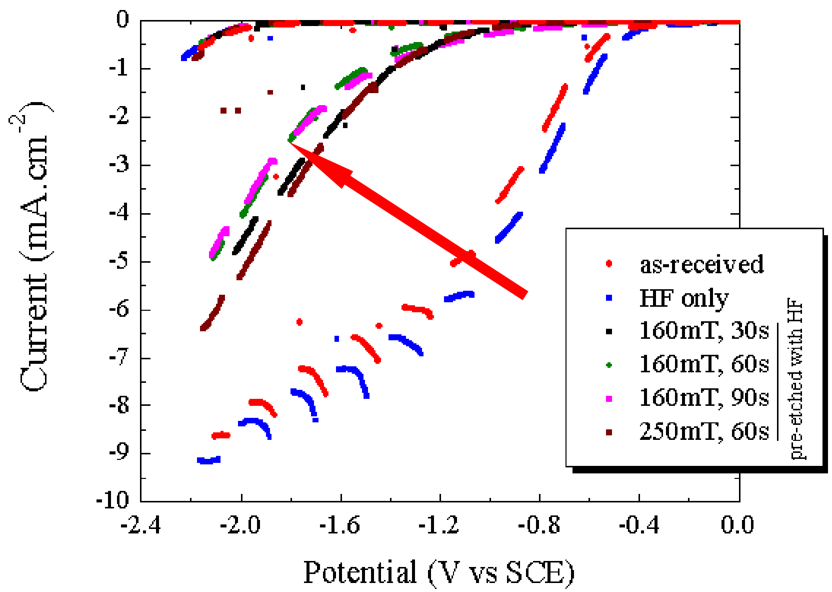
[Data measured by HNEI]

<u>Progress</u>: Surface modification – use of nanoparticles (Pd/Au)

UV-vis of a-SiC p/i without/with Pd/Au nanoparticles



Pd/Au nanoparticles sputtered on a-SiC



J(V) were done in pH2 buffer, RuO_2 CE, SCE ref, AM1.5G

- Little effect of nano-particles on optical properties, mostly on reflection;
- Degradation of performances after Pd/Au nano-particles deposition.
- <u>A barrier at the Pd/Au / a-SiC interface is most likely formed.</u>

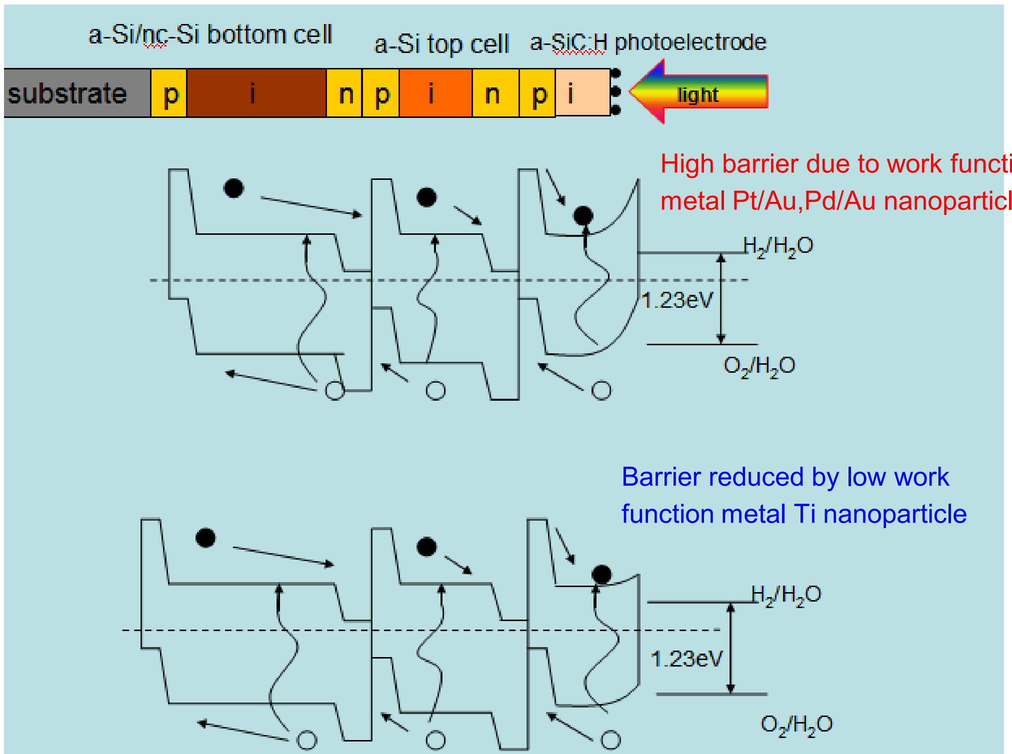
(PdAu work function is close to Au and Pd WF, i.e. approx. 5.4 eV, while a-SiC work function is close Si, approx. 4.6eV)

<u>We need low work function material to improve charge carrier extraction at the a-SiC/electrolyte interface</u>

[Data measured by HNEI]

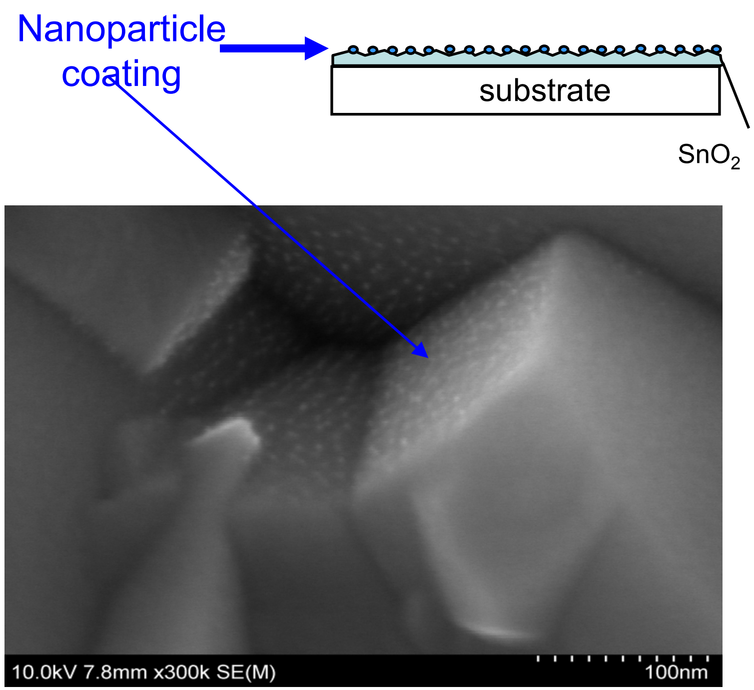
Progress: Surface modification – use of nanoparticles (Ti)

Au, Pt, and Pd possess work functions (WF) greater than 5 eV, which create a barrier as shown in the diagram. Better results have been obtained with titanium nanoparticles (WF = 4.33 eV), which is a close match to a-SiC (WF = 4.6 eV).



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

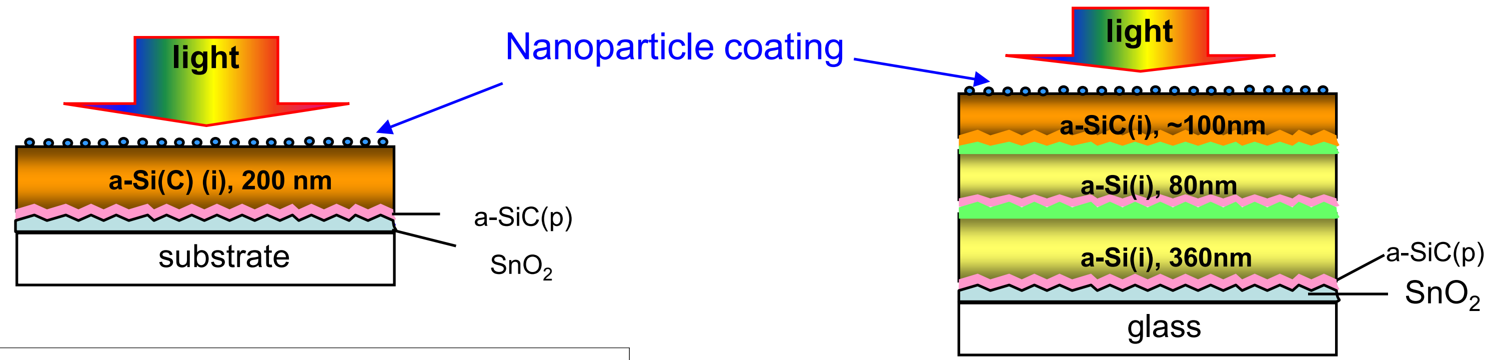
Ti nanoparticles were fabricated using sputtering at room temperature on SnO_2 substrates.

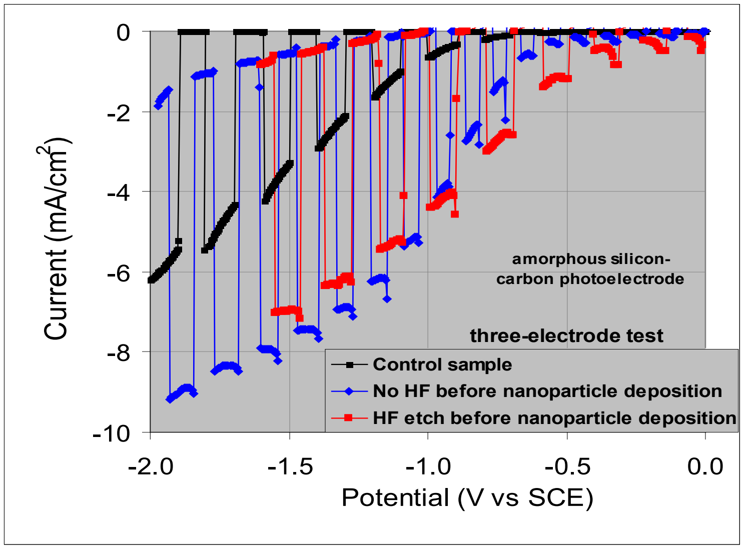


SEM image of the nanoparticles on textured SnO_2

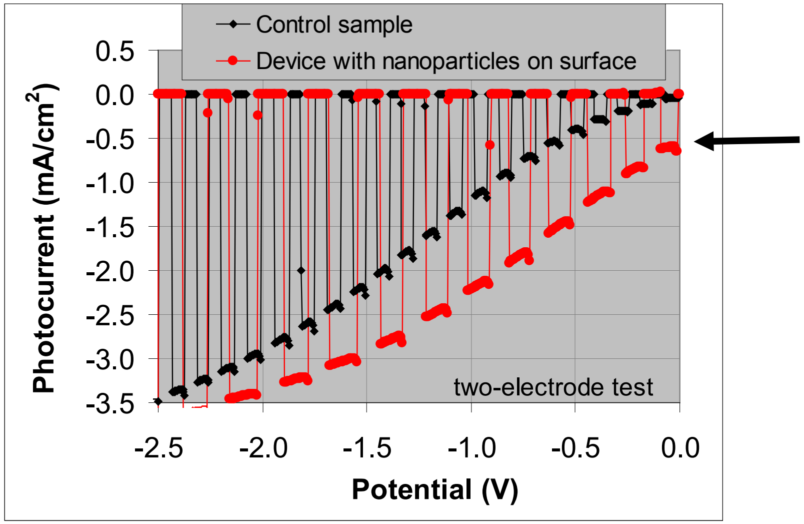
[SEM taken by HNEI]

Progress: Surface modification – use of nanoparticles (Ti)





nanoparticle on a-SiC p/i photoelectrodes
(deposition time=180 sec.)



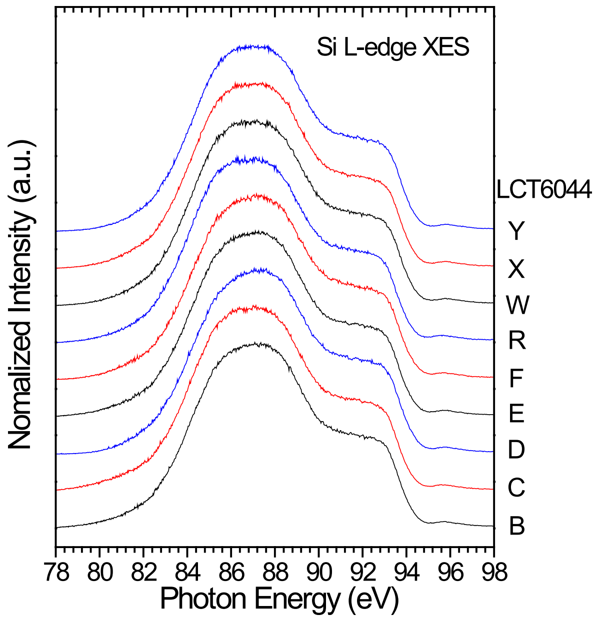
nanoparticle on hybrid PEC device
(deposition time=50 sec.)

- Decrease of hydrogen evolution reaction overpotential
- In hybrid PEC cell Ti nanoparticle formation on the surface helped increase the photocurrent to 0.6 mA/cm^2 at zero external bias.
- **In combination with oxide removal by etching this should lead to >2 mA/cm^2 at zero external bias (i.e STH eff, >3%) .**

[Data measured by HNEI]

Progress: Impact of PEC testing on the bulk material

Electrode Identification Number	Type of Testing	Test Parameters
LCT 6044 B	None	N/A
LCT 6044 C	Low	Sample placed in pH2 PO4 buffer in dark for 24 hrs
LCT 6044 D	Partial Moderate	pH2 PO4 buffer, AM 1.5 illumination, Chopped light 5 times, no electrode attached
LCT 6044 E	Partial Moderate	pH2 PO4 buffer, -2V vs Ref to 0.05V vs Open Circuit sweeping V, no illumination, 3E
LCT 6044 F	Partial Moderate	3E Chopped light IV, pH2 PO4 buffer, -2V vs Ref to 0.05V vs Open Circuit, AM 1.5, Chop at 100 mV increments
LCT 6044 R	Durability	Performed chopped light only at AM 1.5, then 24 hr galvanostatic @ zero applied current under AM 1.5, pH2 PO4 buffer
LCT 6044 W	Partial Moderate	Illuminated OCP, 2 fiber optic illuminators, 3E, pH 2 PO4 buffer, 60s: 20 dark, 20 light, 20 dark
LCT 6044 X	Moderate	Illuminated OCP, 2E IV, and 3E IV
LCT 6044 Y	Partial Moderate	2E Chopped light IV, pH2 PO4 buffer, -2V vs Ref to 0.05V vs Open Circuit, AM 1.5, Chop at 100 mV increments



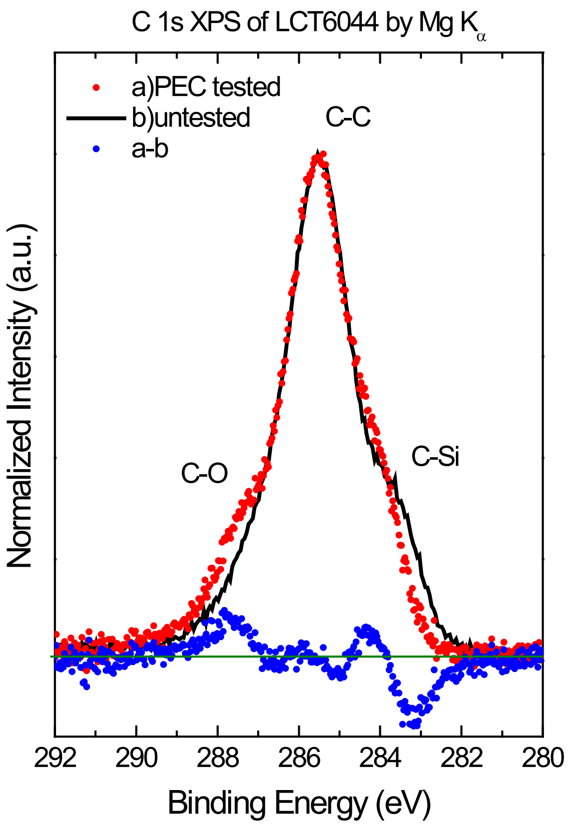
Raw Si L-edge XES spectra of a variety of a-SiC sample untested (B) and after different treatments as listed in the table.

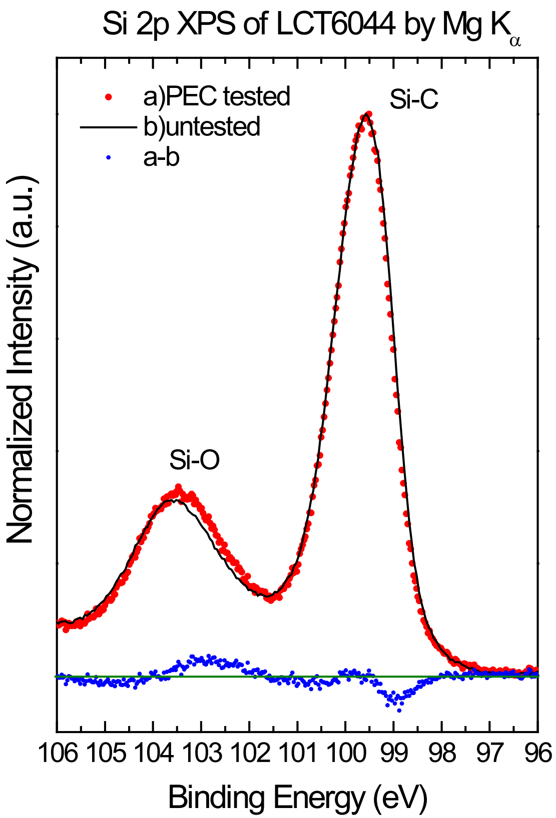
- This measurement provides information on the 3s and 3d occupied partial density of states of Si atoms in the surface-near bulk region (within the first ~100 nm of the surface).

- **The chemical environment of Si atoms in the surface-near bulk region does not change significantly after the test.**

PEC test at NREL, Data measured and analysis by Professor Heske's group at UNLV

Progress: Impact of PEC testing

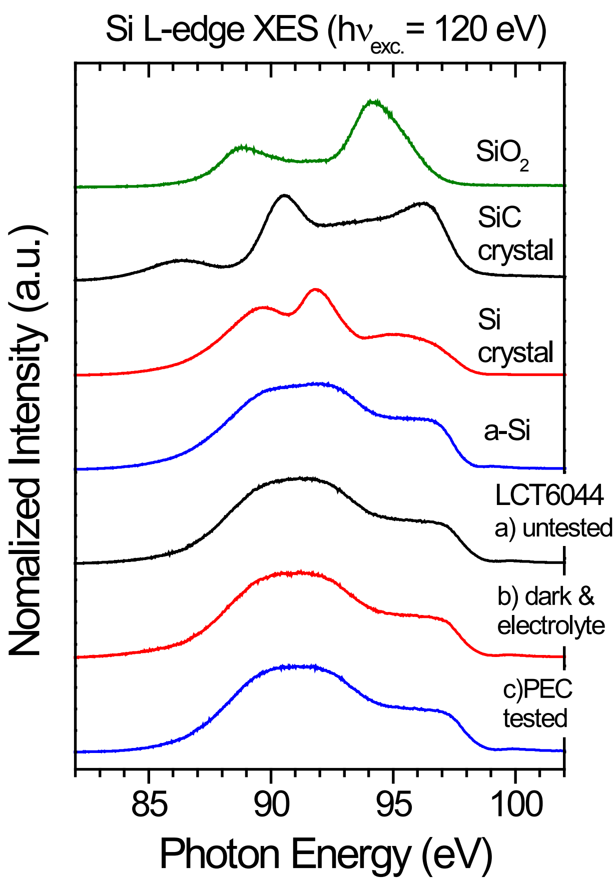


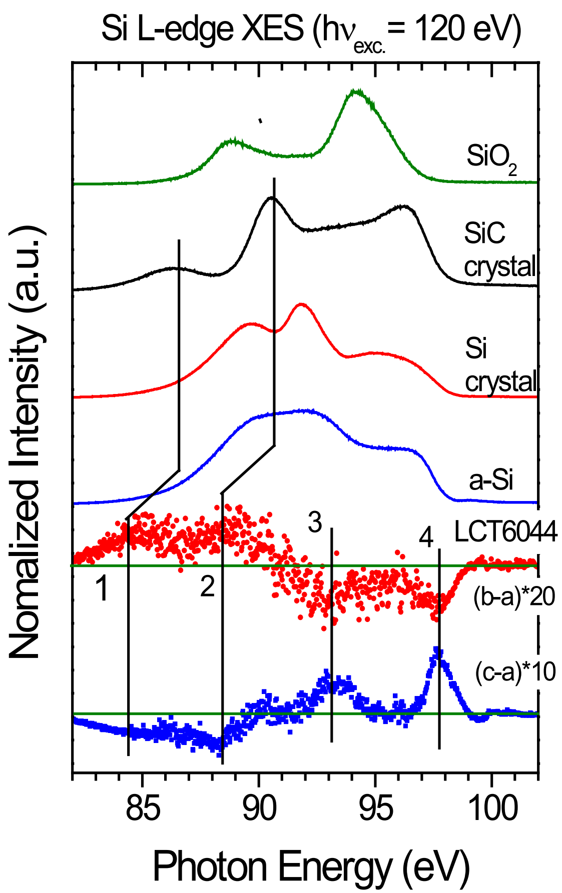


- PEC testing: AM 1.5 ; pH2 H_3PO_4 buffer; at NREL
- After testing, both C-O/C-C and Si-O/Si-C ratios increase
- C-Si/C-C ratio decreases after testing

PEC test at NREL, Data measured and analysis by Professor Heske's group at UNLV

Progress: Impact of PEC testing





- The difference spectra of (b-a) and (c-a) are almost opposite
- Features 1&2 is likely contributed by SiC
- Features 3&4 is likely contributed by SiO_2

More surface-sensitive electron spectroscopy techniques will be employed, such as x-ray photoelectron spectroscopy (XPS), to study the sample surface and the impact of PEC testing on the a-SiC samples

For more detail please see the PD051 provided by Professor Heske

PEC test at NREL, Data measured and analysis by Professor Heske's group at UNLV

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;

  Collaborators

  - University of Nevada at Las Vegas (Academic): collaboration to analyze the surface energy band structure of new photoelectrode materials;
  - Stanford University (Academic): collaboration to perform surface modification.

Research Plan

- 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. Use metal nano-particles for surface modification.
   b. Eliminate thin SiOx layer on the surface

2. Analyze the surface structure of the a-SiC photoelectrode after durability test to understand why the photocurrent of the a-SiC photoelectrode increased while its onset shifted anodically after durability test.
   This work will be in collaboration with UNLV and NREL group.

3. Improve the counter electrode and explore other counter electrode materials

4. Fabricate the a-Si tandem solar cell 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.

Research Plan *(cont'd)*

- ❑ 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.
  - Repeat the durability test for the hybrid PEC device for 200 hours.
  - Extend the durability period to even longer

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

A Go/No Go decision will be made by the end of 2010

Goals for 2011-2012

- ➢ **Photocurrent of 5 mA/cm^2 for 300 hours; cluster-tool fabrication on large area flexible substrates**
- ➢ **Photocurrent of 6 mA/cm2 for 500 hours; PEC devices: 7.5% STH efficiency**

Summary (for a-SiC photoelectrode)

- Photocurrent of the hybrid a-Si tandem solar cell/a-SiC photoelectrode (PEC) cell has been improved from 0.8 mA/cm^2 to ~1.3 mA/cm^2, nearly STH of 2%

- The hybrid PEC cell exhibits excellent durability in pH2 electrolyte for up to ~200 hours (so far tested).

- The PEC hybrid device, in a solid state version, has achieved a current density of $\geq$ 4.5 mA/cm^2 (possible STH efficiency >5.5%).

- Surface modification has shown an initial improvement on hybrid PEC cell, which is very encouraging.

Project Summary

➢Relevancy

MVSystems/HNEI project is accelerating the development of **three important PEC thin-film materials classes** (a-SiC, WO_3 and CGSe) with high potential for reaching DOE goals for 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.

-Establish test protocols for screening of PEC materials.

Hurdle #1: Opto-electronic properties (Eg, dark and light conductivity, Fermi level position, extended state/hopping conduction) to match a set of predetermined criteria.

Hurdle #2: Basic solid state Schottky barrier device for extraction of current

Hurdle #3: Use semiconductor/electrolyte techniques at HNEI to match a set of predetermined criteria.

➢Progress

Items	Thin-film materials	2008			2009-2010		
		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		2.9 mA/cm^2	90%		3.6 mA/cm^2	90%
	CGSe		20 mA/cm^2	**100%**		20mA/cm^2	**100%**
Material/Device durability	a-SiC	≥ 100 hours	150 hours	**100%**	≥ 200 hours	200 hours	**100%**
	WO_3		100 hours	**100%**		100 hours*	50%
	CGSe		10 hours*	10%		10 hours*	5%
Device STH efficiency	a-Si/a-SiC	≥ 3.7%	1%	25%	≥ 5%	1.6% *(6% projected from solid-state device perf.)*	32%
	WO_3		3.1%	85%		3.1% *(4.4% projected using 4-junction configuration)*	62%
	CGSe		0%	0%		0% *(5% projected using 4-junction configuration)*	0%

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) Improve band diagram understanding 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 performance of the thin-film solar cell used in the hybrid PEC device.

(6) Esatablish and implent screening of PEC materials to lead to STH >10%

Hurdle #1: Opto-electronic properties (Eg, dark and light conductivity, Fermi level position, extended state/hopping conduction) to match a set of predetermined criteria.

Hurdle #2: Basic solid state Schottky barrier device for extraction of current

Hurdle #3: Use semiconductor/electrolyte techniques at HNEI to match a set of predetermed criteria.

(7) Additional materials evaluation: nc-SiC, a-SiCN, nc-SiNx, a-SiON.

A Go/No Go decision will be made by the end of 2010