

*Midwest Optoelectronics*

# **Critical Research for Cost-effective Photoelectrochemical Production of Hydrogen**

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Toledo, Ohio

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Project ID # PDP 34

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## Timeline

- Project start date: 10/13/2004
- Project end date: 10/12/2007
- Percent complete: 30%

## Budget

- Total project funding
  - DOE share: \$2,921,501
  - Contractor share: \$760,492
- Funding received in FY05: \$100,000
- Funding received in FY06: \$200,000
- Funding for FY07: \$400,000, \$200,000 for NREL

## Barriers addressed

- DOE MYPP Objective for PEC
  - By 2015, demonstrate direct PEC water splitting with a plant-gate hydrogen production cost of \$5/kg projected to commercial scale.
- Technical Targets:
  - 2010: STH Eff > 9%; Durability >10,000 hours; Cost < \$22/kg
  - 2015: STH Eff > 14%; Durability >20,000 hours; Cost < \$5/kg
- PEC Hydrogen Generation Barriers -- MYPP 3.1.4.2.3
  - M. Materials Durability
  - N. Materials and Systems Engineering
  - O. PEC efficiency

## Partners

- |  |                  |
|--|------------------|
| ➤ University of Toledo                 | Dr. Xunming Deng |
| ➤ National Renewable Energy Laboratory | Dr. John Turner  |
| ➤ United Solar Ovic Corp.              | Dr. Jeff Yang    |

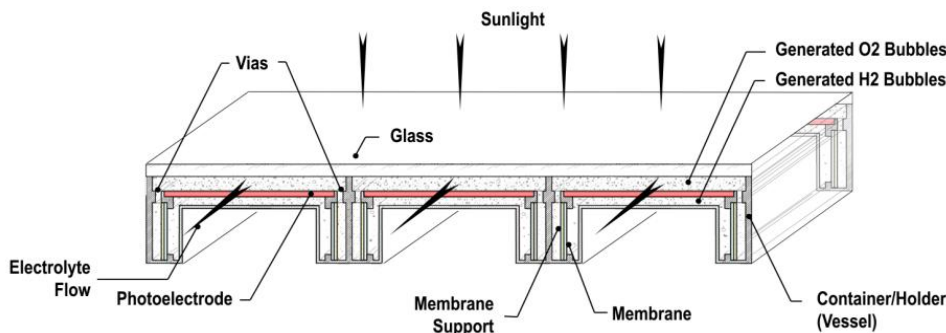
# Objectives

- To develop critical technologies required for cost-effective production of hydrogen from sunlight and water using thin film-Si based photoelectrodes.
- To develop and demonstrate, at the end of the 3-year program, tf-Si based PEC systems with 9% solar-to-hydrogen efficiency with a lifetime of 10,000 hours and with a potential hydrogen cost below \$22/kg.

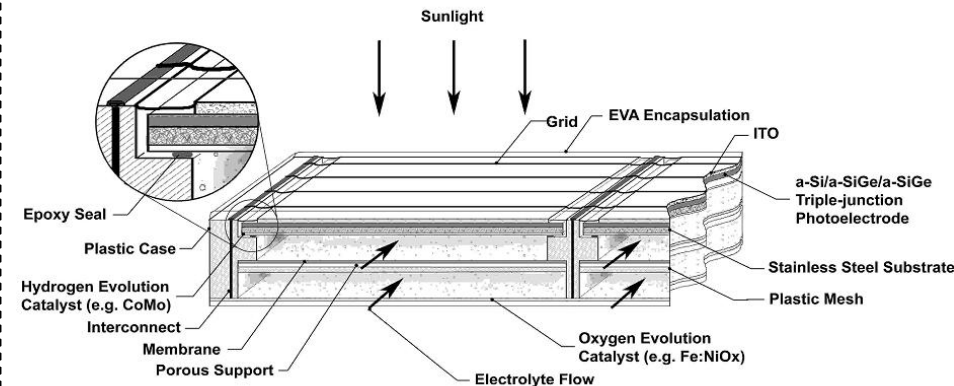
# Approaches

Two approaches are taken for the development of efficient and durable photoelectrochemical cells.

An immersion-type PEC cells



A substrate-type PEC cell



# Research Tasks

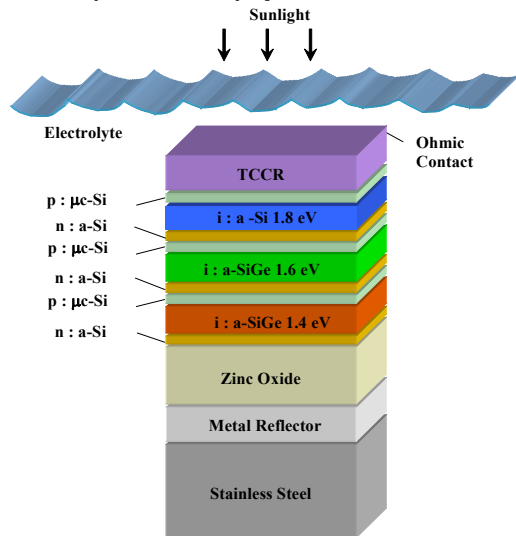
- Task 1: Transparent, conducting and corrosion resistant coating for triple-junction  $\text{tf-Si}$  based photoelectrode
- Task 2: Hybrid multijunction PEC electrode having semiconductor-electrolyte junction
- Task 3: Understanding and characterization of photoelectrochemistry
- Task 4: Fabrication of low-cost, durable and efficient immersion-type PEC cells and systems
- Task 5: Fabrication of large-area, substrate-type PEC panels

# Approaches for PEC electrodes

Two separate approaches for the development of high-efficiency and stable PEC photoelectrode for the immersion-type PEC cells:

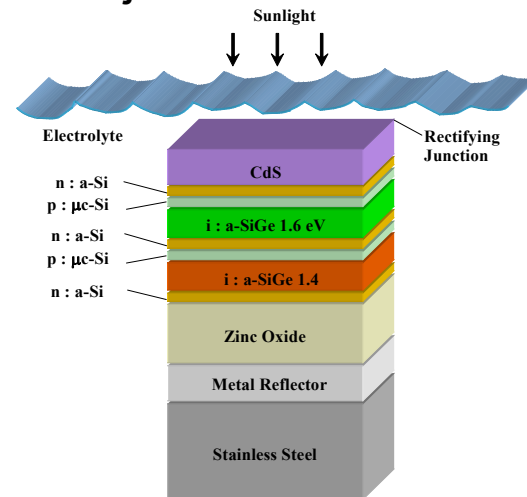
## Approach 1A (Task 1):

- Develop triple junction tf-Si photoelectrodes covered with a transparent, conductive, and corrosion resistant (TCCR) protection layer



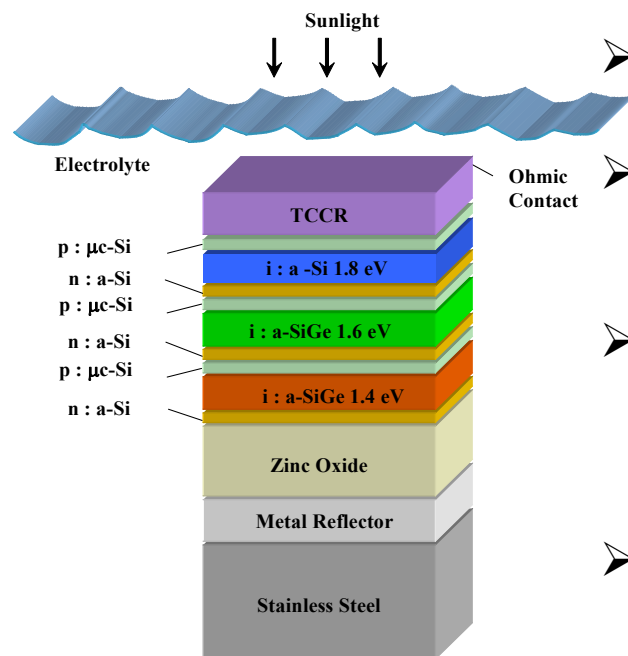
## Approach 1B (Task 2):

- Develop hybrid, triple junction photoelectrodes with a semiconductor-electrolyte junction as the top junction and tf-Si alloys as the middle and bottom junctions



# Task 1: TCCR Layer for Triple-Junction tf-Si Photoelectrode

A triple-junction tf-Si based solar cells (a-Si/a-SiGe/a-SiGe or a-Si/a-SiGe/nc-Si) are used to generate the voltage bias and a transparent, conducting and corrosion resistant (TCCR) coating is deposited on top to protect the semiconductor layer from corrosion while forming an ohmic contact with the electrolyte



## Materials and Process

### Requirement for TCCR

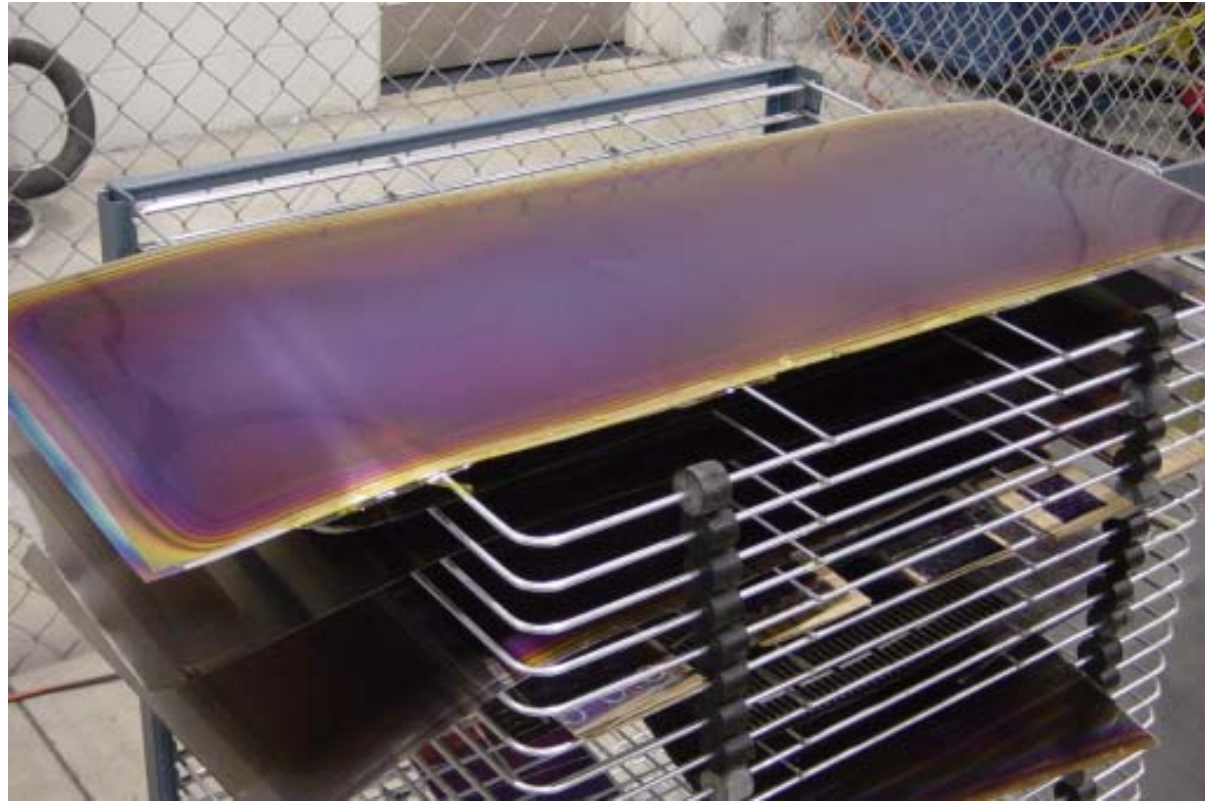
- High transmission – to allow photons reach the solar cells
- High conductivity – to allow electron transfer to/from electrolyte
- High chemical and electrochemical stability – to protect the solar cell from being corroded
- Low cost – to reduce the overall system cost
- Low temperate deposition (below 250 °C) – so that the a-Si layers deposited earlier would not degrade.



# Major Activities under Task 1

- Fabrication of triple-junction a-Si/a-SiGe/a-SiGe solar cells (Photoelectrodes)
- Fabrication of triple-junction a-Si/a-SiGe/nc-Si solar cells (Photoelectrodes)
- Deposition of transparent, conducting and corrosion-resistant coating using sputtering
- Optimization of a sputter system with four linear targets (4"x15"), capable of making TCCR films on 1 ft x 4ft substrates.

# Optimization of large-area sputter system

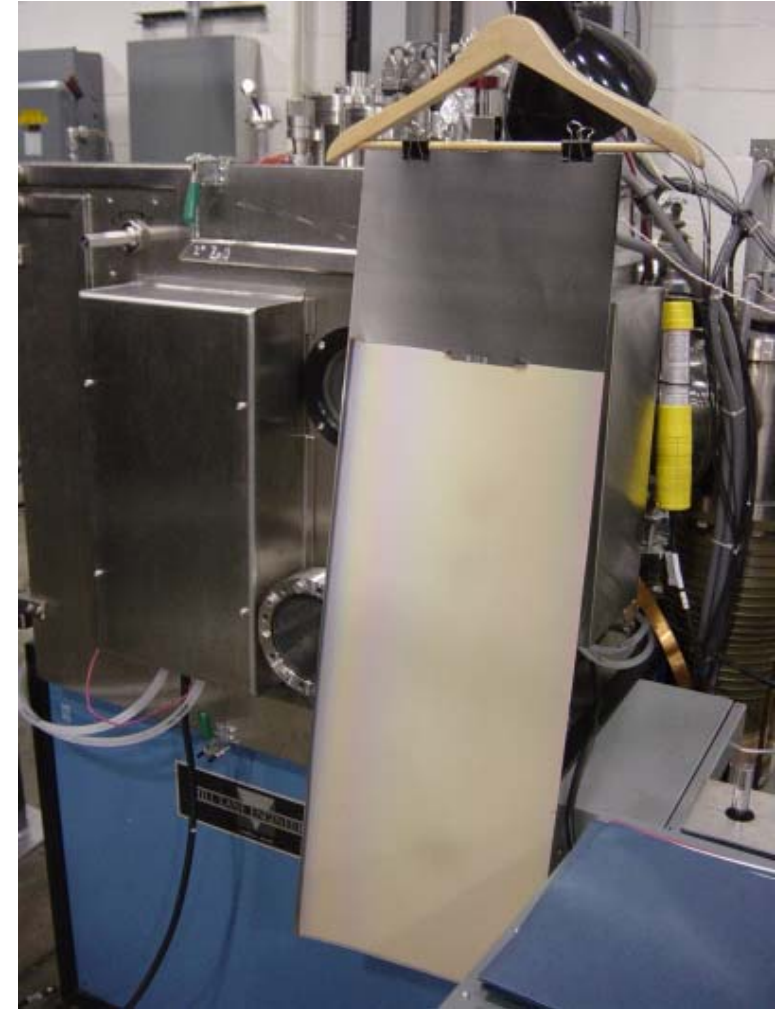


Optimization of a sputter system with four linear sputter guns to make TCCR layer on 1 ft x 4ft substrates. Shown in the right photo are substrates coated with Indium Tin Oxide.

# Large-Area Sputter System

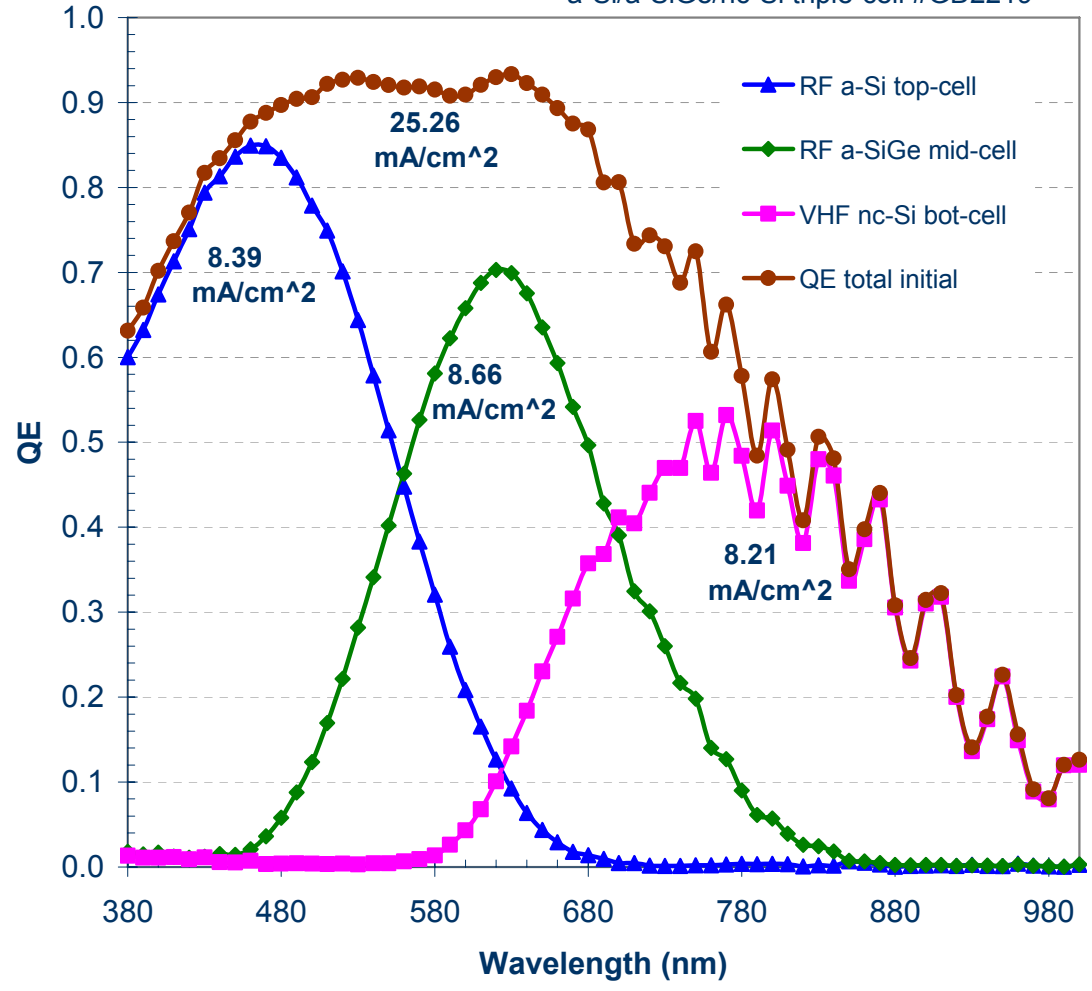


Large-area 4-gun sputter system for coating of oxide films. Shown in the right photo is zinc oxide coated on stainless steel.



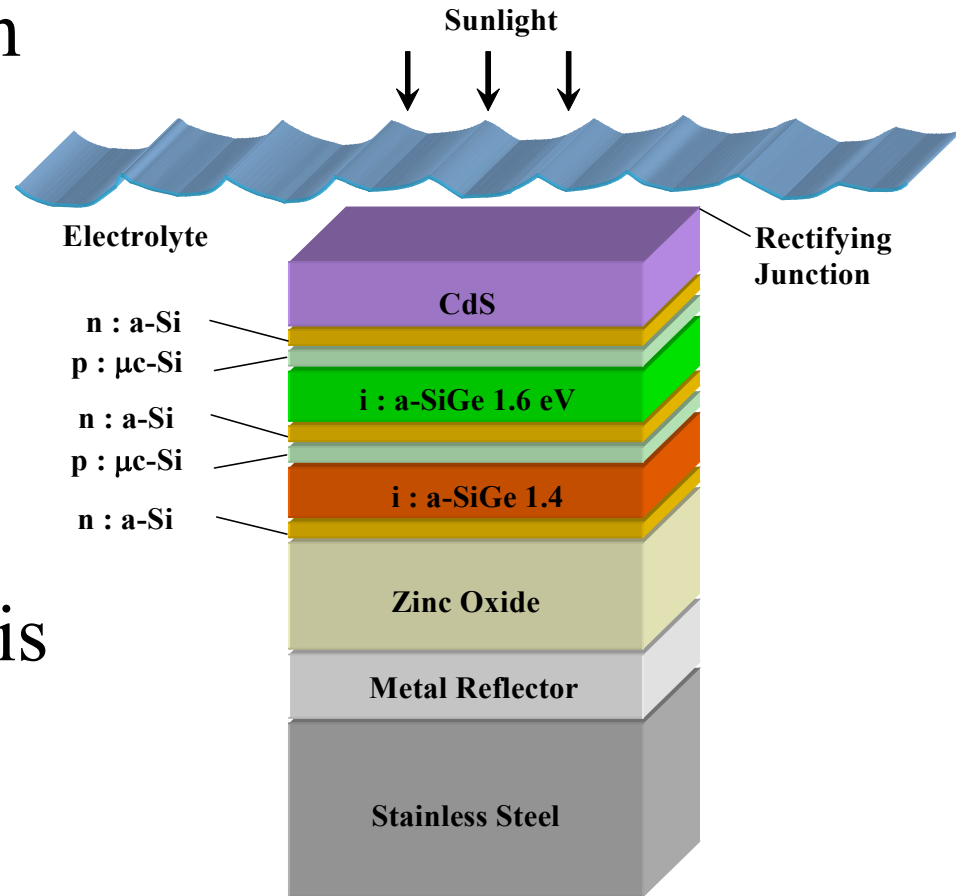
# Triple-junction Photoelectrodes

a-Si/a-SiGe/nc-Si triple-cell #GD2219



Quantum efficiency curves of improved triple-junction a-Si/a-SiGe/nc-Si photoelectrodes

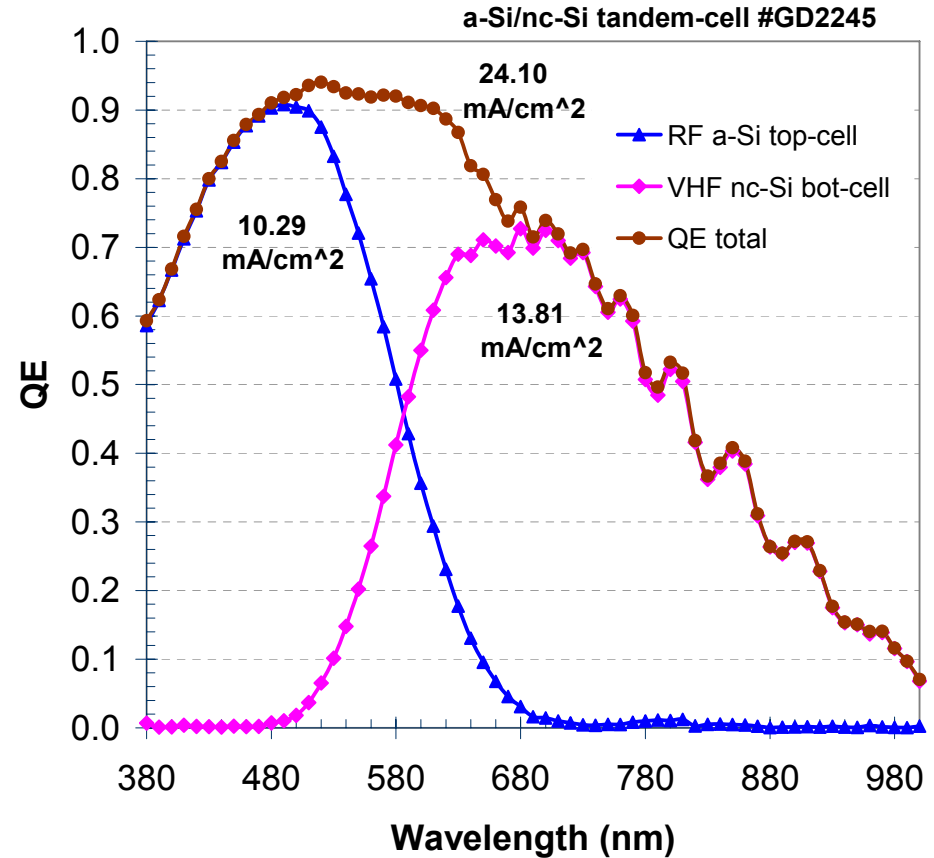
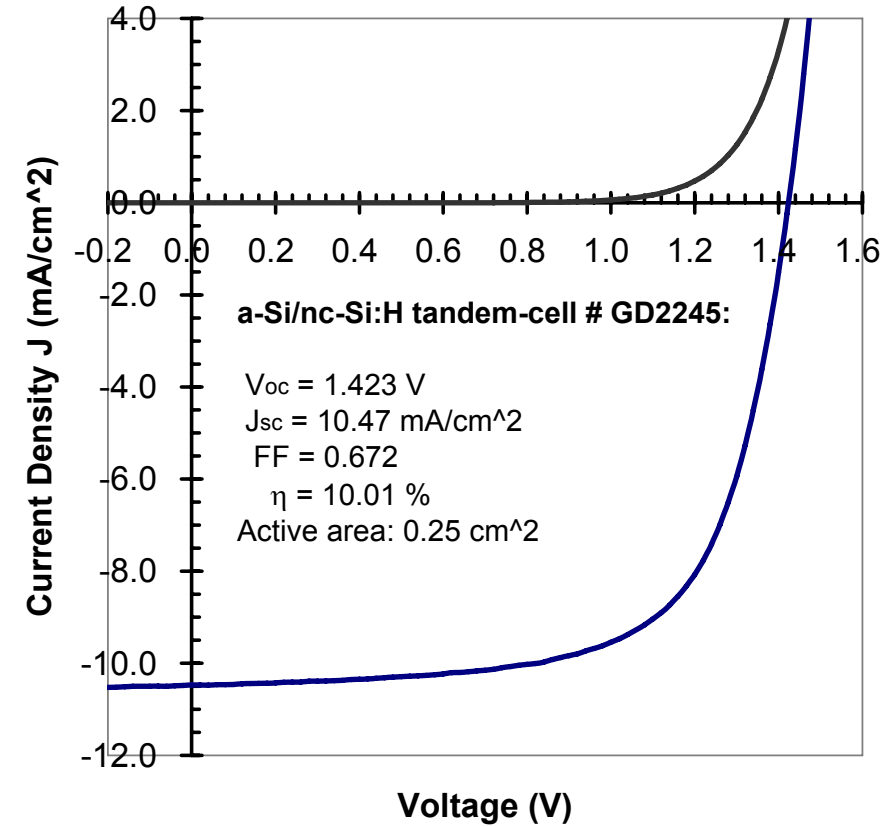
A hybrid structure in which two  $\text{tf-Si}$  based junctions (middle and bottom junctions of the present triple-junction  $\text{tf-Si}$  cell) provide a voltage bias (around 1.1V) and a third junction (the top junction) is a rectifying junction between a photo-active semiconductor (PAS) and the electrolyte.



## Major Activities under Task 2

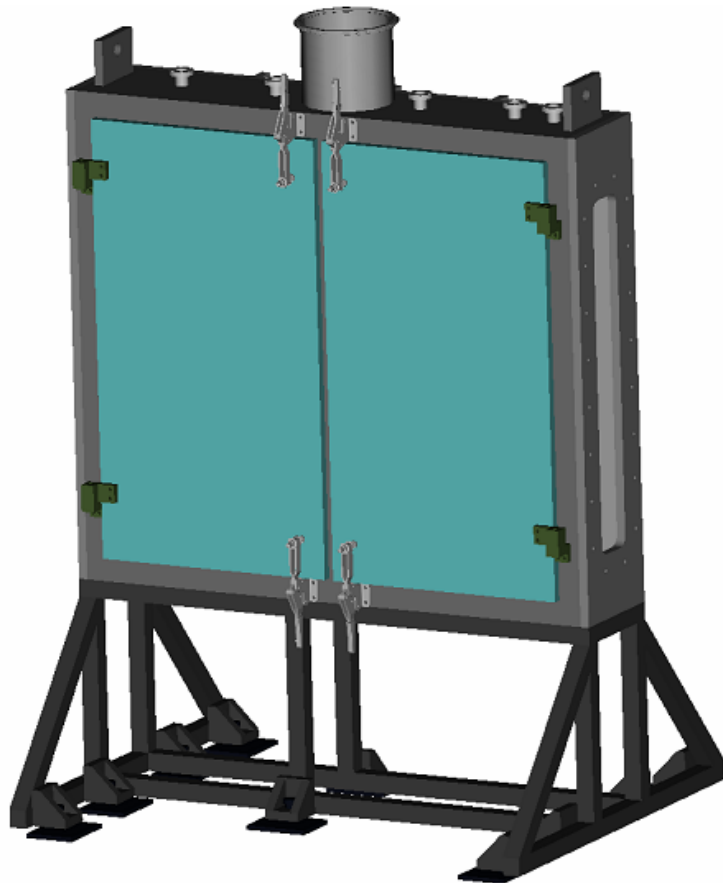
- Fabrication of double-junction a-SiGe/a-SiGe solar cells (photoelectrode)
- Fabrication of double-junction a-SiGe/nc-Si solar cells (photoelectrode)
- Deposition of photoactive semiconductor layer for semiconductor-electrolyte junction
- Construction of large-area sputter system to make photoactive semiconductor layers in large area

# 10% a-Si/nc-Si tandem-junction solar cell



➤  $\eta = 10.01\%$  initial efficiency ( $V_{oc} = 1.423\text{V}$ ,  $J_{sc} = 10.47 \text{ mA/cm}^2$ ,  $FF = 0.672$ ) was achieved for a-Si/nc-Si tandem-junction solar cells on UT-BR substrate with SS/Al/Ag/ZnO structure.

# Large-area sputter system



- Designed a large area sputter system capable of making photoactive semiconductor layers on 3 ft x 3ft substrates.
- System has already been custom made by outside vendor according to MWOE supplied engineering drawings.
- System can be used to make oxides and metal layers for PEC electrodes.



## Task 3: Understanding and Characterizing PEC

- Several efforts are on going under this Task.
- NREL team is currently developing improved understanding of PEC process for a-Si based photoelectrodes.
- An outdoor solar testing facility has been installed and used for outdoor testing of PEC panels
- Large-area IV tester has been purchased.
- Large-area environmental chamber has been installed and used to test long-term durability and failing mechanism for PV and PEC panels.



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# MWOE Outdoor Solar Testing Facility



MWOE's outdoor solar testing facility for testing PEC hydrogen production



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# Large-Area I-V Tester Purchased



Keithley 2420  
Sourcemeter  
Voltage/Current source  
and measuring unit for  
obtaining computerized  
current-voltage  
characteristics of larger  
area PEC panels.

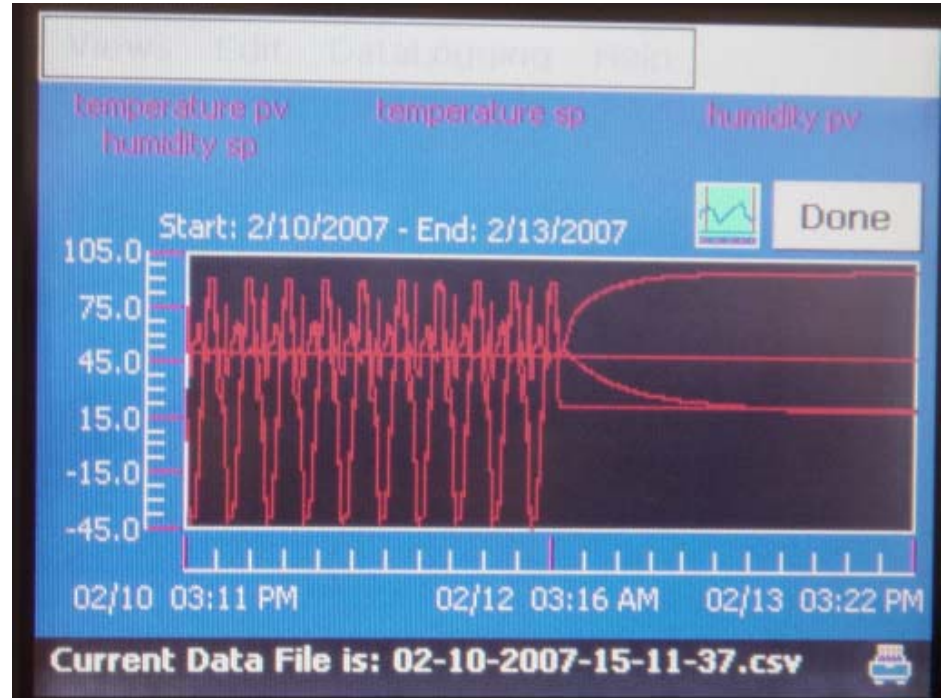


Spire 4600 Series large area solar simulator, purchased using cost-share funds, will allow accurate characterization of the active component of large-area PEC panels up to 200 cm x 137 cm (6.5' x 4.5') in size.



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# Environmental Test Chamber Installed



Screenshot of environment chamber controller, showing multiple temperature cycles between minus 40 and +90 degrees Celsius.

(Temperature on vertical axis.)



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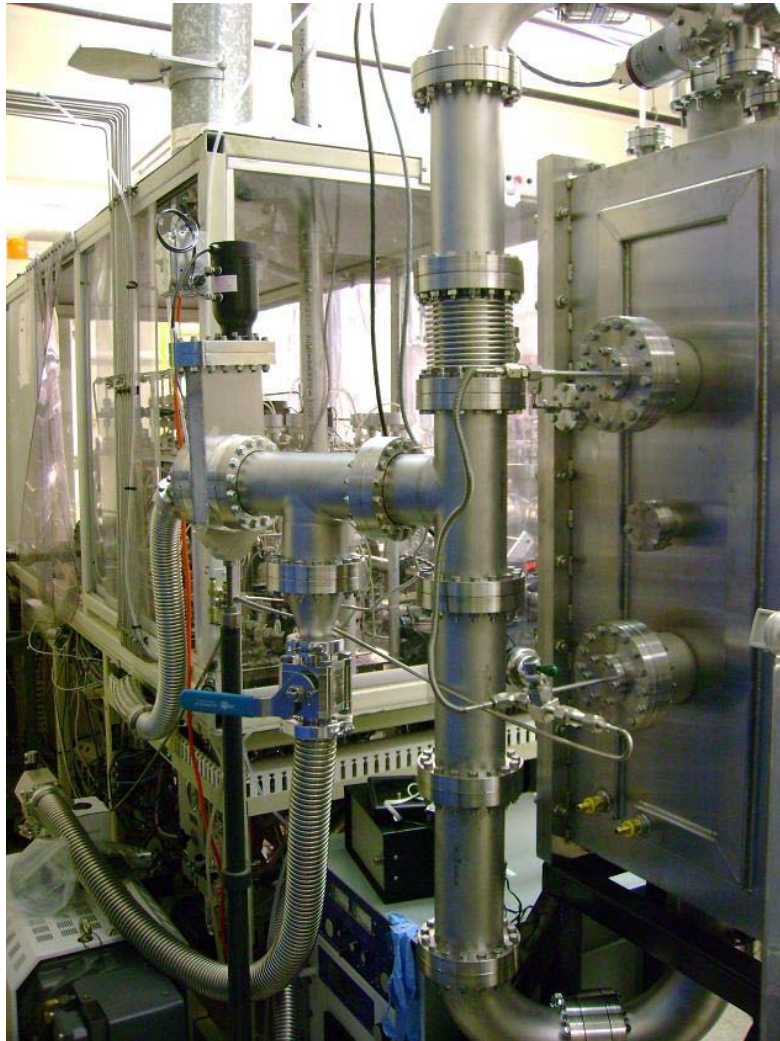
## Task 4: Immersion-type PEC cell

- Focus on Task 4 is on the construction and optimization of deposition system that will be used for making large-area photoelectrode for immersion-type PEC cells
- Designed and constructed a system capable of making 1ft x 3ft photoelectrodes
- Improved deposition uniformity over large area
- Continued the design and optimization of immersion-type PEC cells



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# New System for Depositing Photoelectrodes



1 ft x 3 ft a-Si photoelectrodes from new PECVD system



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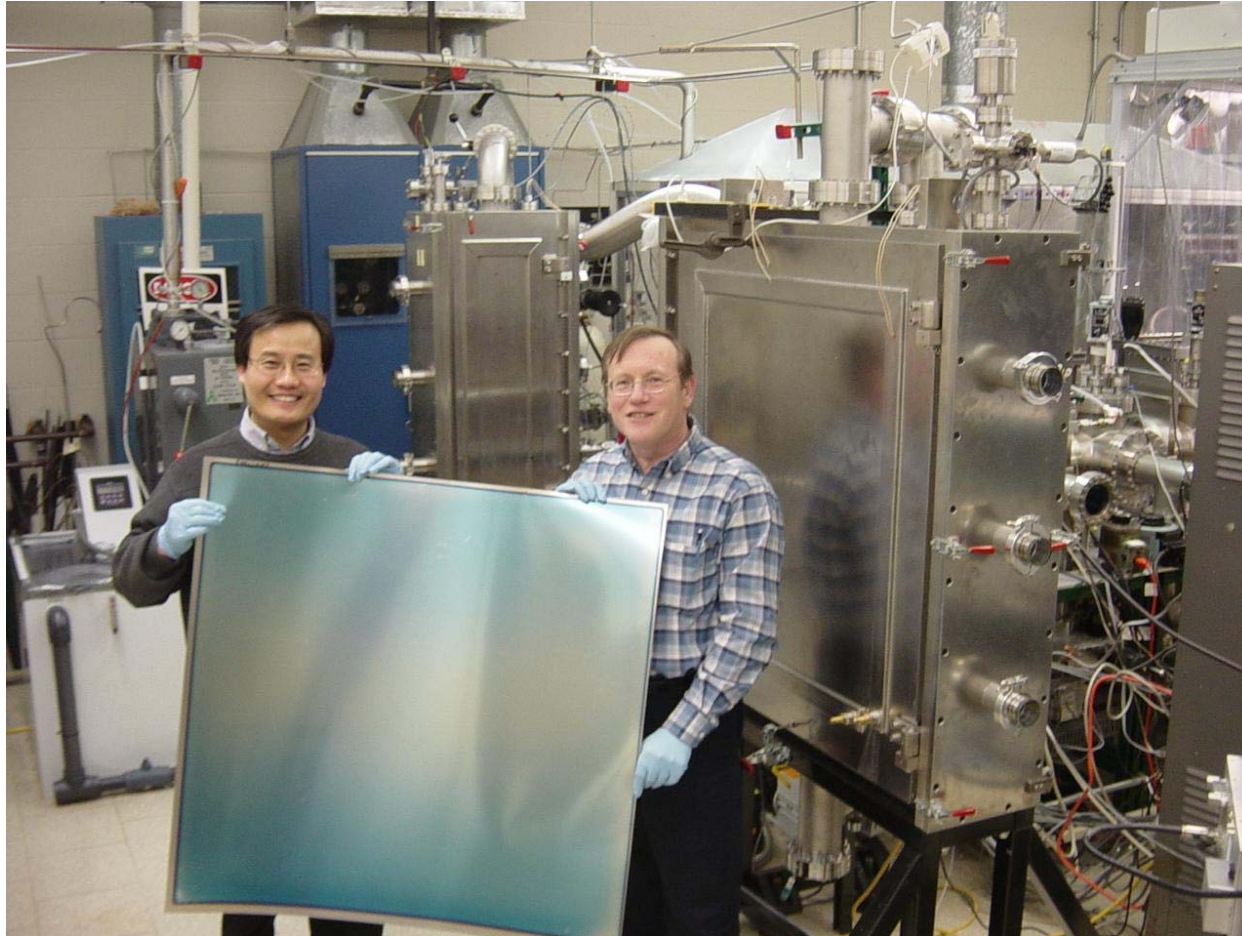
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# New System for Depositing Photoelectrodes



A second new PECVD system, capable of making 3 ft x 3ft photoelectrodes have been designed and constructed. Amorphous Si photoelectrodes (solar cells) have been fabricated in this new system.

# Task 5: Fabrication of Substrate-Type PEC cells

- Focus under this task has been on establishing facilities to make substrate-type PEC cells in large area.
- Designed and built a computer-controlled process for application of current-conducting grids in the substrate-type PEC cells
- Designed and built a fabrication facility for making substrate-type PEC electrodes.
- Designed, developed and constructed a photo-assisted electrochemical shunt passivation system to remove shunts and shorts in the photoelectrodes.





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# Newly Developed Fabrication Facility for Substrate-type PEC Electrodes



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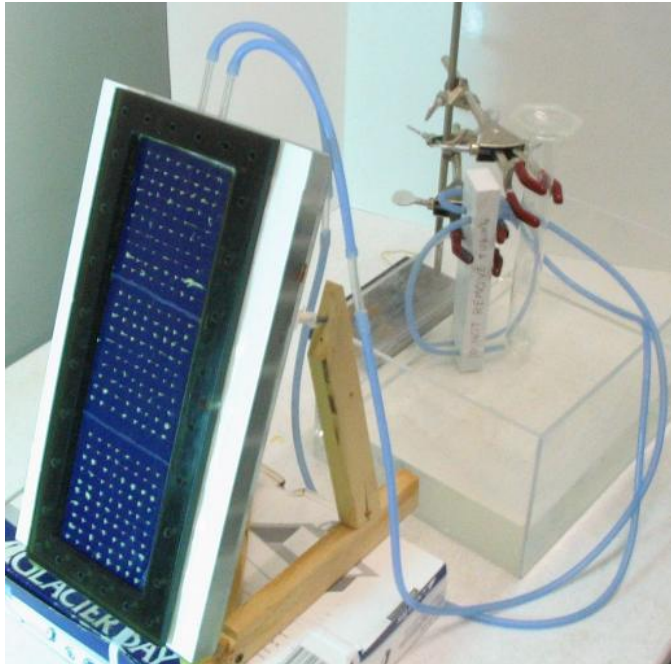


# Shunt/Short Passivation Process



Developed a system to do shunt passivation using a photo-assisted electrochemical process. This process pin points the current-leaking shorts/shunts and convert the conductive oxide around the shorts/shunts into insulator, thereby electrically isolate such shorts/shunts.

# Hydrogen Production Rate



Previously reported PEC Cell:  
Sample size: 4"x12"

H<sub>2</sub> production rate: 6.2 cc/min  
under 0.82 sun intensity.

STH Efficiency: ~5%

We have previously reported substrate-type PEC cell with solar-to-hydrogen production efficiency of ~5%. The improved facility will allow MWOE to make larger PEC panels (e.g. 3ft x 3ft).



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# Future Work

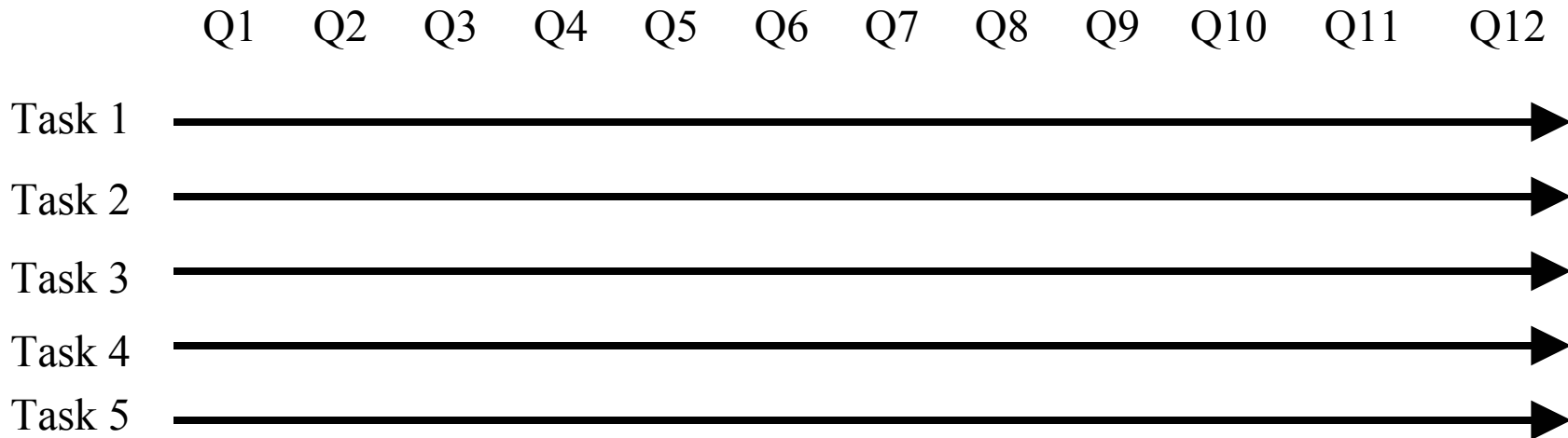
Task 1: Transparent, Conducting and Corrosion Resistant coating for triple-junction tf-Si based photoelectrode

Task 2: Hybrid multijunction PEC electrode having semiconductor-electrolyte junction

Task 3: Understanding and Characterization of photoelectrochemistry

Task 4: Fabrication of low-cost, durable and efficient immersion-type PEC cells and systems

Task 5: Fabrication of 8ft<sup>2</sup>, substrate-type PEC panels



Effort will continue under all tasks.



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# Team Members

- **Midwest Optoelectronics, LLC**

Liwei Xu, Jason Day, Ken Draeger, Jason Justice, Mark McGilvery, Marty McClanahan, Richard Podlesny, Stanley Rubini, Aarohi Vijh, Carol Williams, Michael Yang

- **University of Toledo:**

Xunming Deng, Alvin Compaan, Robert Collins, Dean Giolando, Maria Coleman and A.H. Jayatissa, Mahabala Adiga, William Ingler, Ling Hu

- **National Renewable Energy Laboratory**

John Turner

- **United Solar Ovonic Corp.**

Jeffrey Yang



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