Midwest Optoelectronics

Critical Research for Cost-effective Photoelectrochemical Production of Hydrogen

Liwei Xu

Midwest Optoelectronics LLC

Toledo, Ohio

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Project ID # PDP 12

This presentation does not contain any proprietary or confidential information

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Overview

Timeline

- Project start date: 10/13/2004
- Project end date: 10/12/2007
- Percent complete: 15%

Budget

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

Barriers Addressed and Partners

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 Ovonic 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.

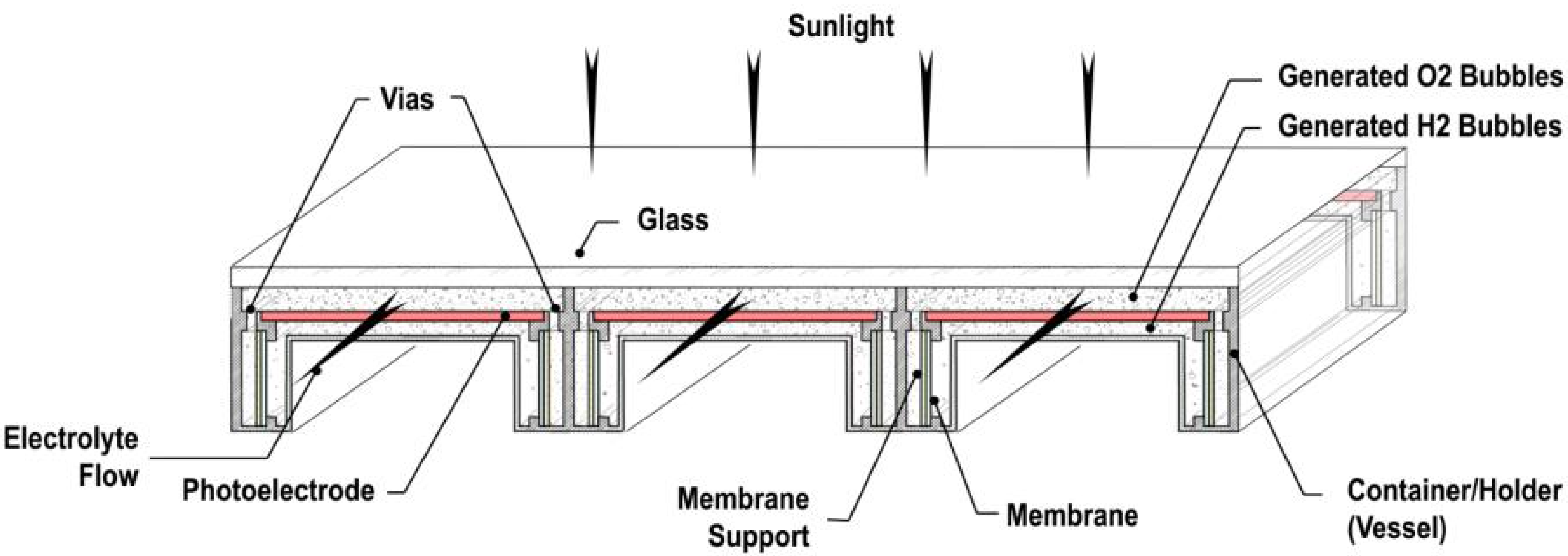
- To develop and demonstrate, at the end of the 3-year program, tf-Si based PEC systems with 9% solar-to-hydrogen efficiency with a lifetime of 10,000 hours and with a potential hydrogen cost below $22/kg.

Background

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

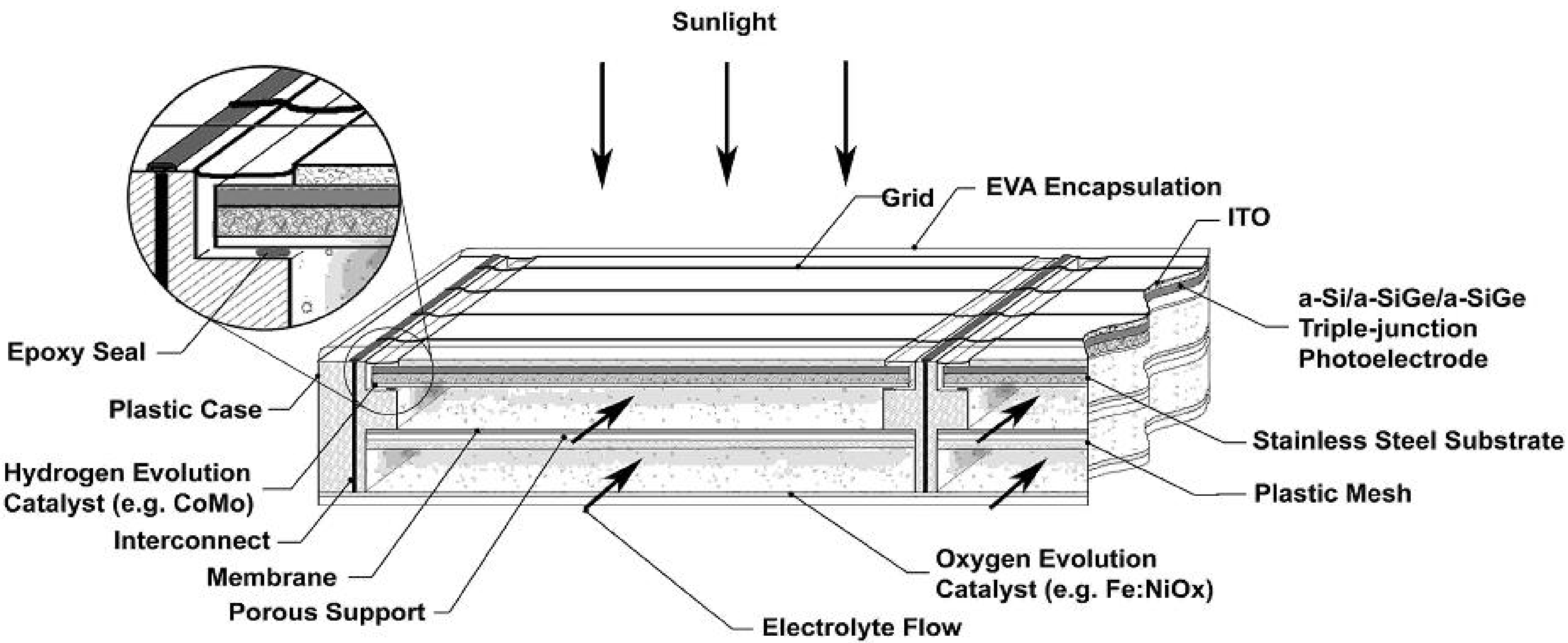
- An immersion-type photoelectrochemical cells
  - Photoelectrode is immersed in electrolyte
- A substrate-type photoelectrochemical cell
  - Photoelectrode not in direct contact with electrolyte

Approach 1 – Immersion-type PEC cell



Approach 2 – Substrate-type PEC cell

Substrate Type



Research Tasks

- 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 large-area, substrate-type PEC panels

Approaches for PEC electrodes

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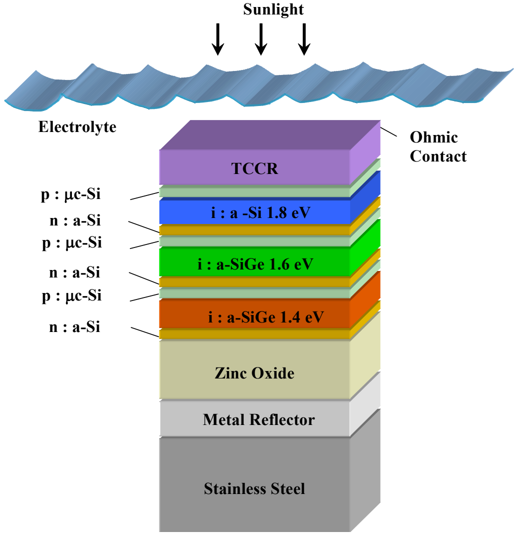
Two separate approaches for the development of high-efficiency and stable PEC photoelectrode for the immersion-type PEC cells:

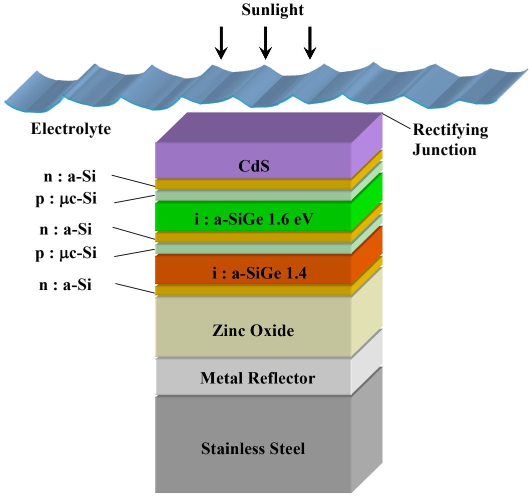
Approach 1A (Task 1):

- 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



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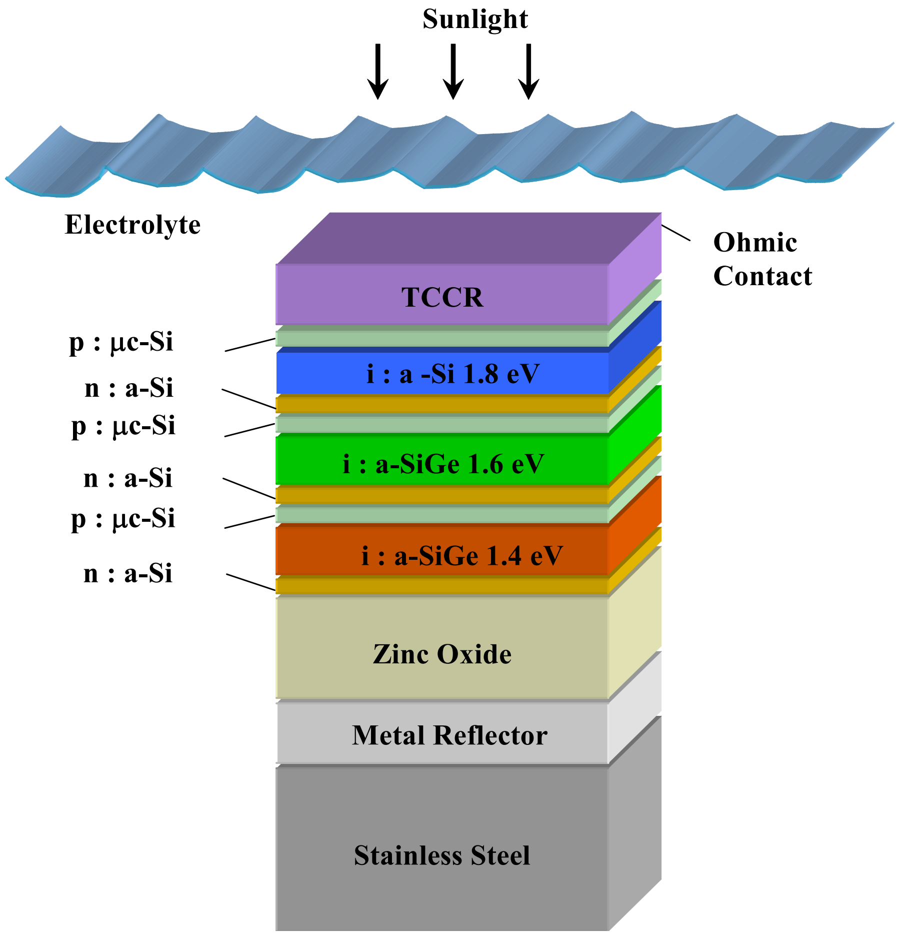
Task 1: TCCR Layer for Triple-Junction tf-Si Photoelectrode

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



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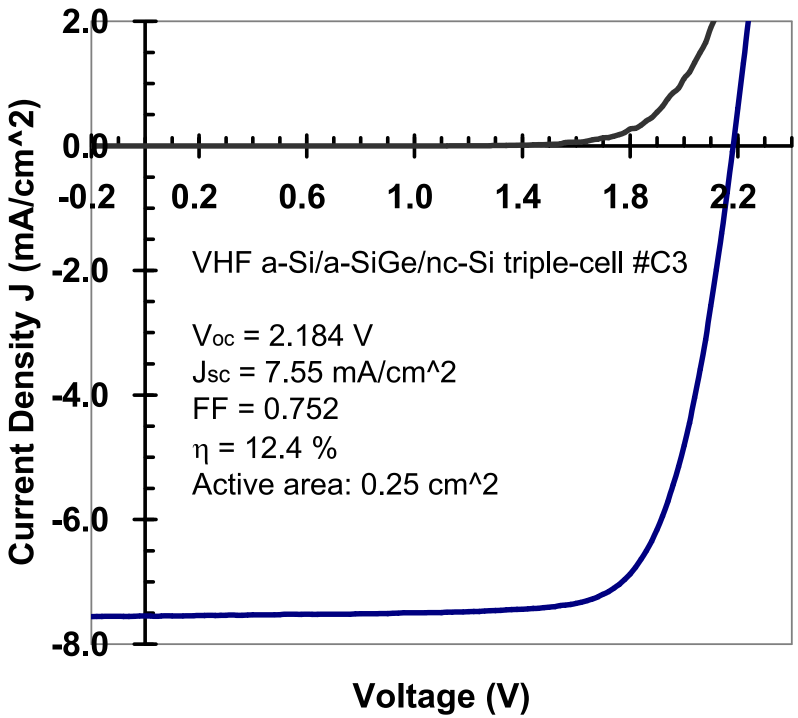
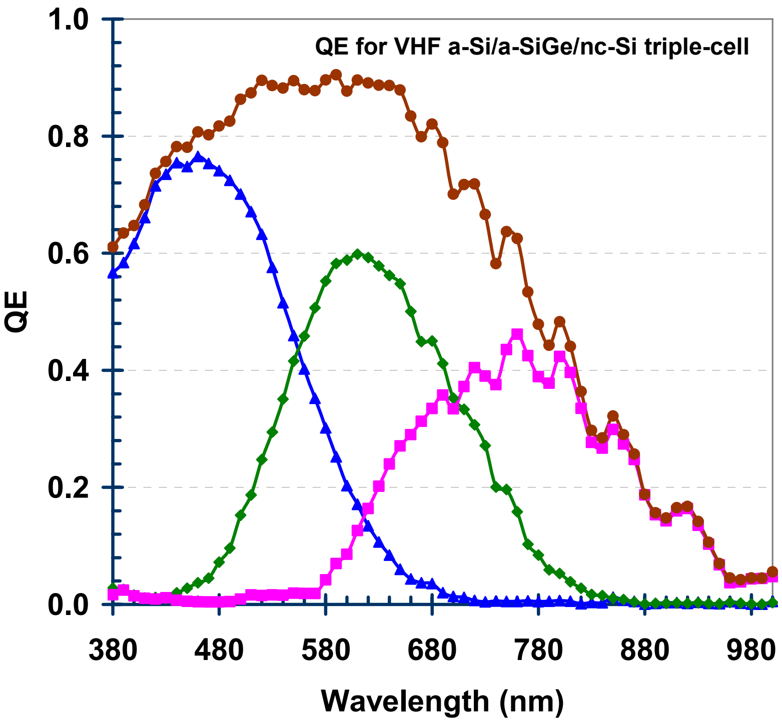
Major Activities under Task 1

- 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

a-Si/a-SiGe/nc-Si Solar Cells





- Using nc-Si:H cell as component bottom-cell, 12.4% initial and 11% stable cell efficiencies in a-Si/a-SiGe/nc-Si triple-junction structure have been achieved.
- Very good FF of 0.752 for triple-junction cell using nc-Si:H cell as current-limited cell.
- Work done at UT using funds partially provided by NREL

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Deposition of transparent, conducting and corrosion-resistant coating using sputtering

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 ^{o}C) – so that the a-Si layers deposited earlier would not degrade.

Fluorine doped tin oxide (SnO_2:F) as TCCR coating

- Selection of Sputter Process:
  - sputtering a target that contains Sn, O and F (selected)
  - reactive sputtering of SnO_2 in an Ar/F_2 atmosphere (not selected due to corrosion issue)
- Selection of Sputter target
  - Co-sputtering from SnO_2 target and SnF_2 target -- Process not selected, since it is extremely difficult to make SnF_2 sputter target
  - Sputter deposition of SnO_2/SnF_2 -- Process selected and a target with SnO_2:SnF_2 of 75:25 is used.
  - Co-sputter from SnO_2/SnF_2 and SnO_2 targets -- This allows us to vary the fluorine composition in SnO_2:F.
- Status:
  - Discussed with various target vendors. Chosen CERAC.
  - Used a three-gun deposition system.
  - First sets of SnO_2:F have already been completed. Currently waiting for analysis.

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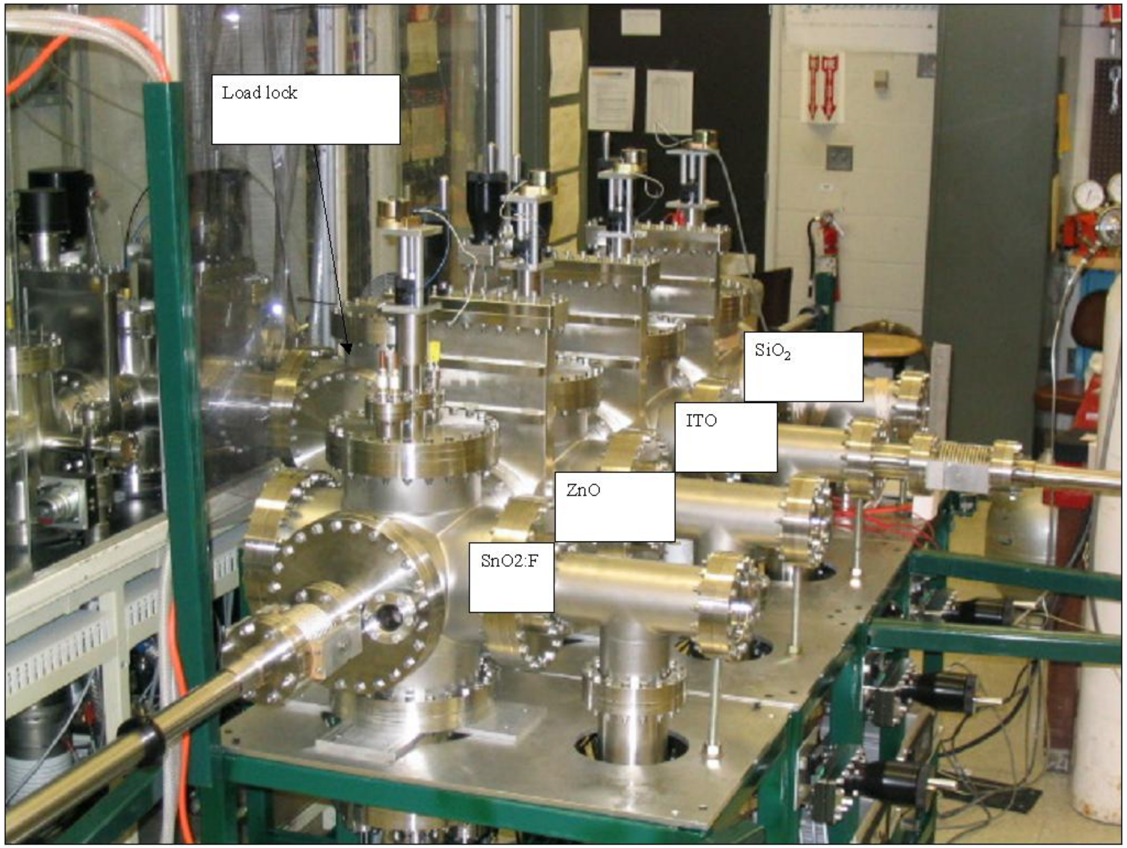
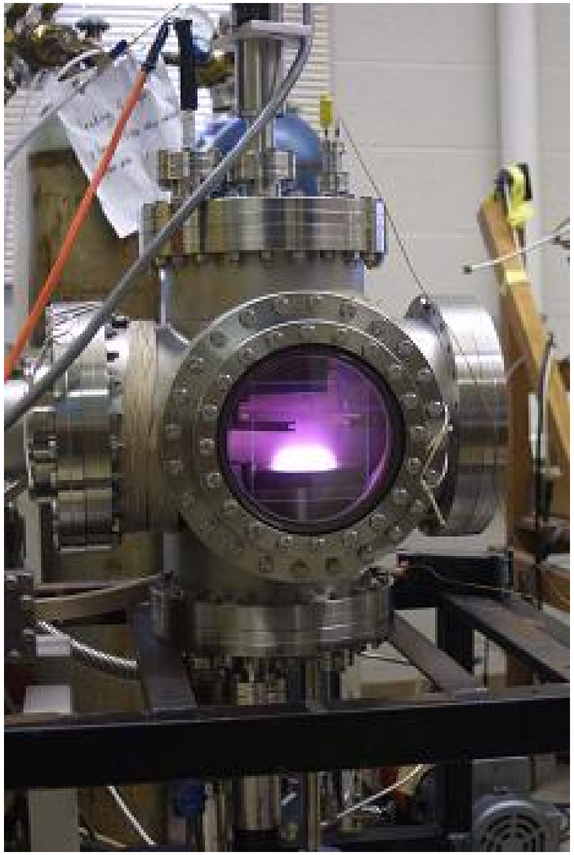
Sputter Deposition Process for TCCR Coating





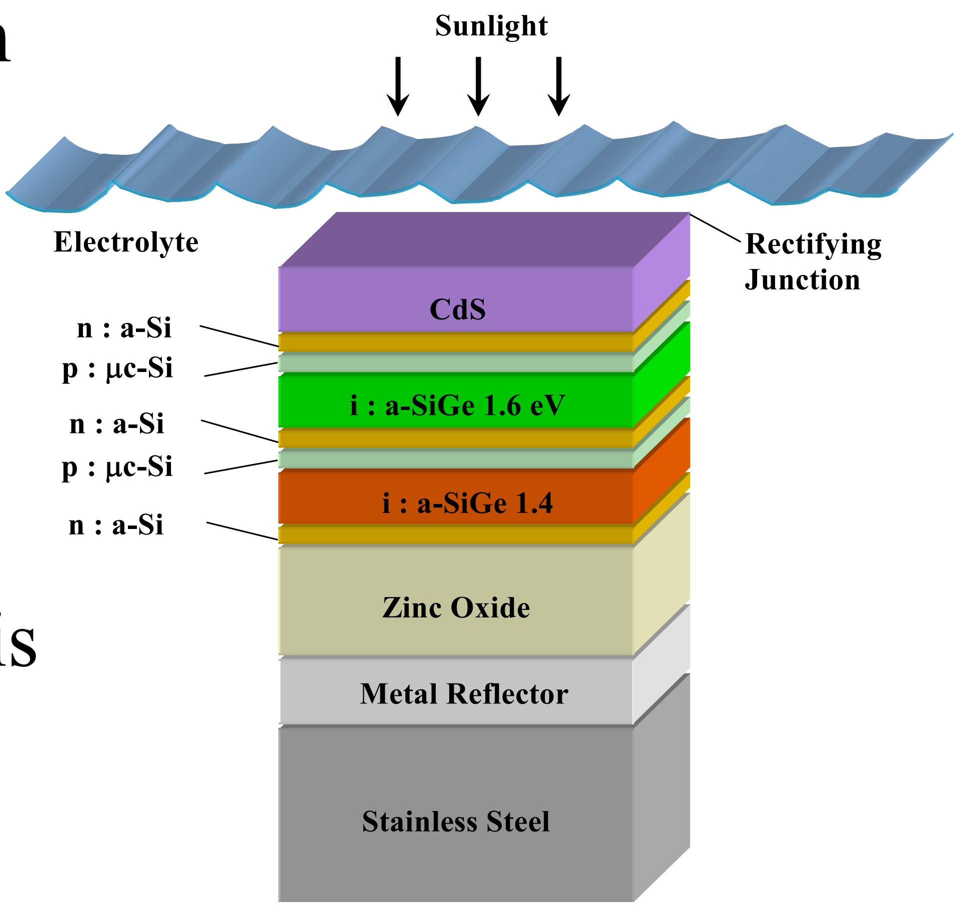
UT cluster tool system having multiple sputter deposition chambers for the deposition of TCCR coatings

Scaling up the thin film deposition process

- Restored and set up a large-area sputter deposition system (donated to the University of Toledo by Ford Motor Company) that could allow the sputter deposition of TCCR materials over large area, 1 ft x 4ft on a flexible substrate.
- Redesigned the sputtering magnet arrangement to enhance the sputter deposition rate
- Established the auxiliary components, cooling, power supplied etc, for the system capable of making TCCR coatings in large area
- Work supported using cost-share funds provided by the State of Ohio.

Task 2: Hybrid PEC Photoelectrodes

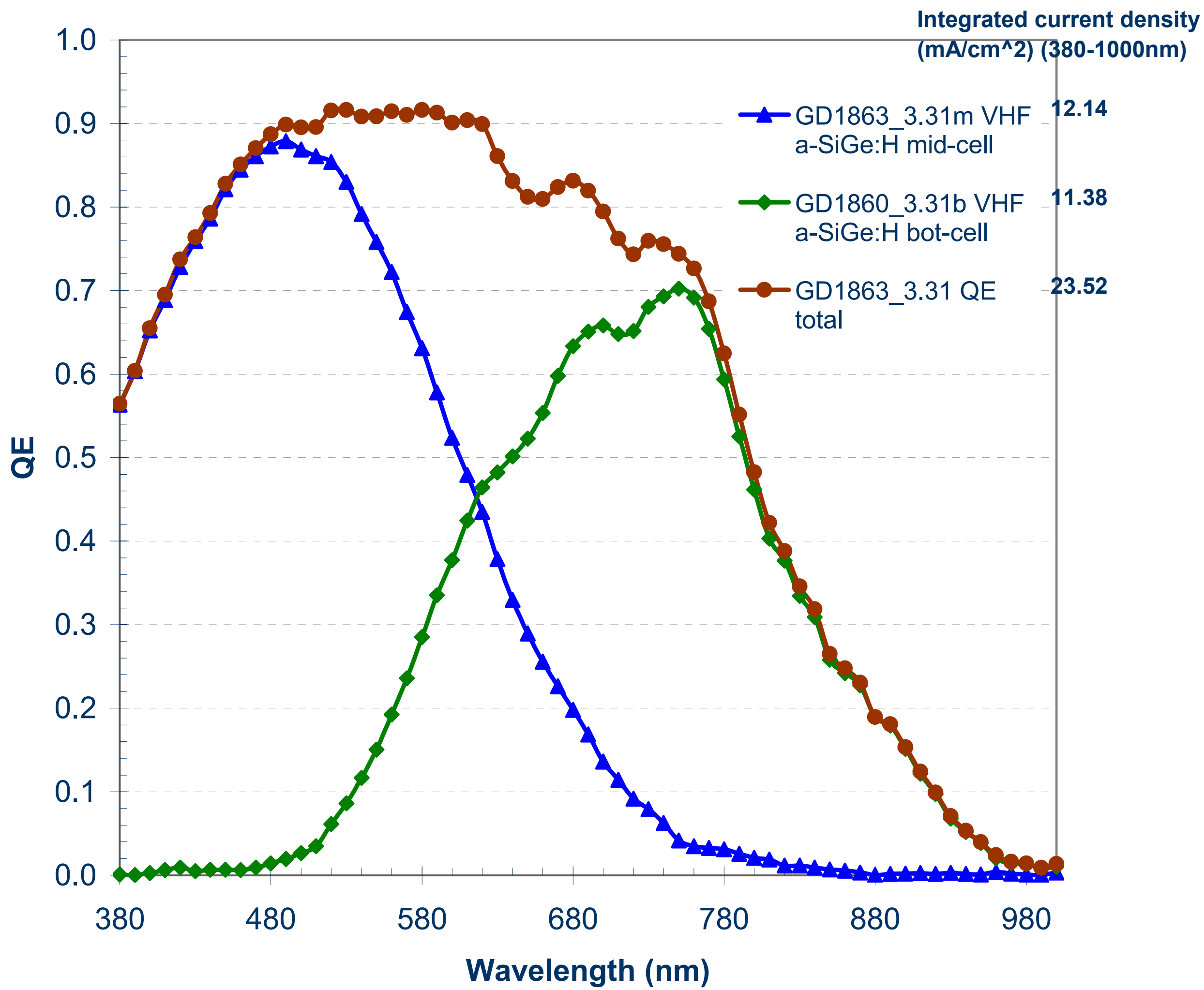
A hybrid structure in which two tf-Si based junctions (middle and bottom junctions of the present triple-junction tf-Si cell) provide a voltage bias (around 1.1V) and a third junction (the top junction) is a rectifying junction between a photo-active semiconductor (PAS) and the electrolyte.



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

a-SiGe/a-SiGe double junction solar cell



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a-Si/nc-Si double junction solar cell

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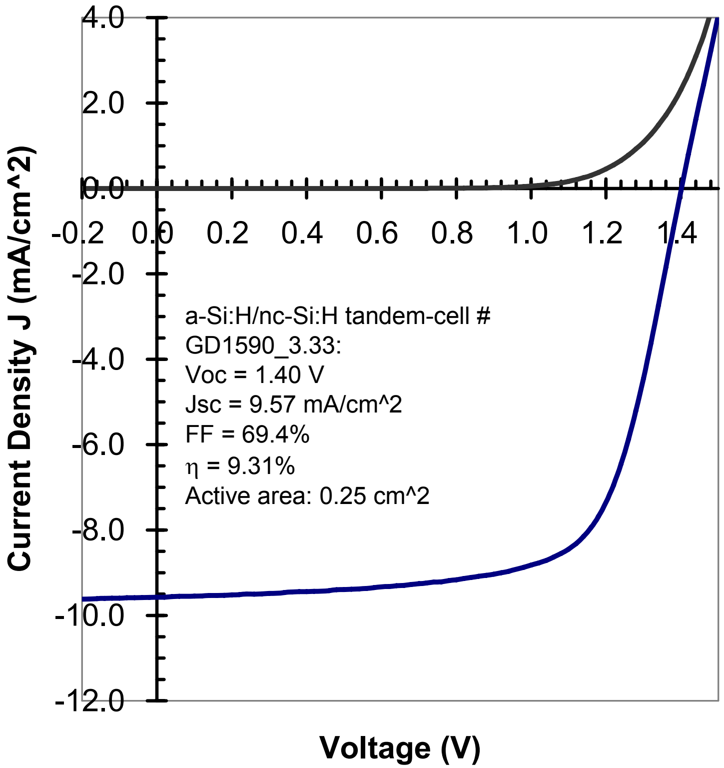

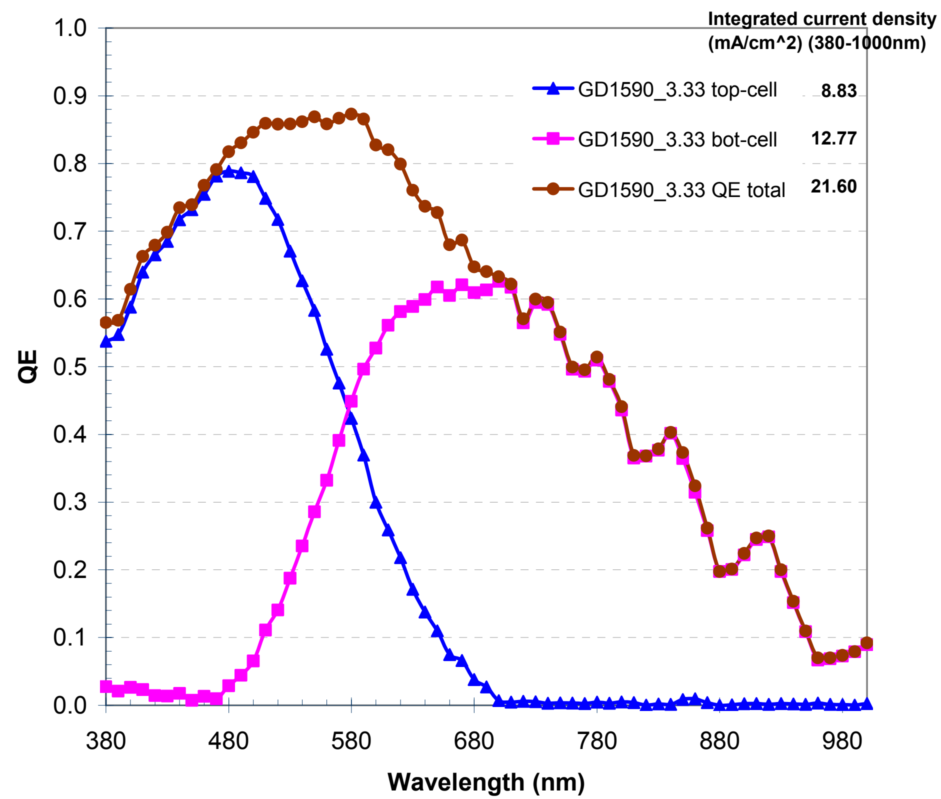

- ➢Preliminary effort on VHF a-Si/nc-Si tandem-cell with efficiency of 9.3%. A thick top-cell is expected to get a current-match.
- ➢Work done at UT using funds partially provided by NREL

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Sol-Gel Deposition of Photoactive Semiconductor materials

- Spin coated sol-gels of **tin oxide** coating
  - prepared from the pre-cursor Tin(II) 2-ethylhexanoate
  - [CH3 (CH2)3 CH(C2H5)CO2]2 Sn
  - Varied temperature
  - Varied duration of curing for multiple dip/spin coatings.

- Example:
  - glass slides were dipped in the precursor solution
  - dried for 30 minutes at 100 -150 ^oC to remove the excess solvents
  - spin coated at 5000 RPM for 25 seconds
  - 15 minutes at 400 - 450 ^oC

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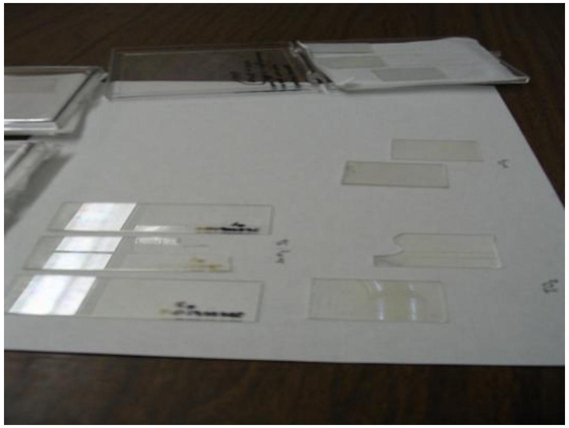
Sol-Gel for Tin Oxide

- Results:
  - good transparency (94.5% to 97.5%)
  - conductivity was high
  - multiple dip or spin coating of pre-cursor solution before heat treatment improved conductivity significantly without drastically reducing the optical transmission.



Sol-gel coating of titanium dioxide

- Procedures
  - pre-cursor Titanium (IV) 2-ethylhexanoate, 97 % with molecular formula Ti[OOC(C2H5) CH(CH2)3 CH3]4 with molecular weight 623.75
  - films were prepared from 20 % weight of the above solution in EtOH.
  - coating were prepared with pretreatment at 150-200 ^{o}C for 20 minutes
  - then cured at 400 – 450 ^{o}C for 90 minutes for single dip coating, 45 minutes for double dip coating.

- Results
  - 94.5 % optical transparency for triple spin coated **$\underline{TiO_2}$** film
  - The electrical resistance was high

Task 3: Understanding and Characterizing PEC

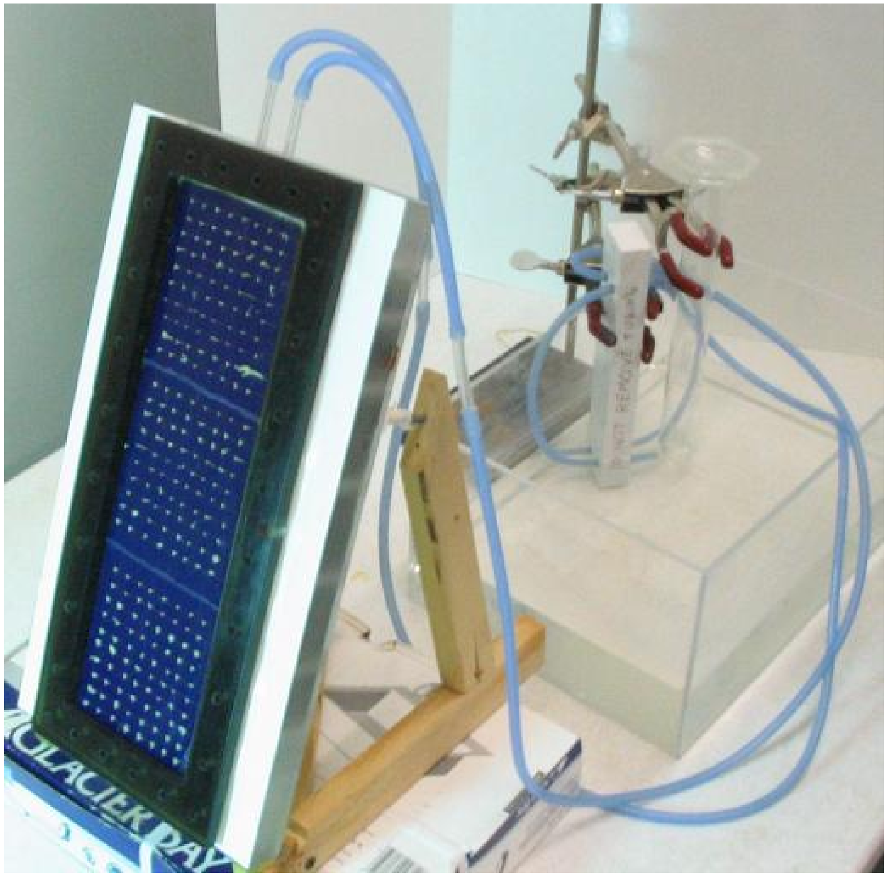
- Several efforts are on going under this Task.
- National Renewable Energy Laboratory is currently developing improved understanding of PEC process for a-Si based photoelectrodes.
- A new light fixture is being installed. This light fixture allows 1000W illumination.
- A 30ft by 40ft area outdoor testing facility has been installed for outdoor testing of PEC panels

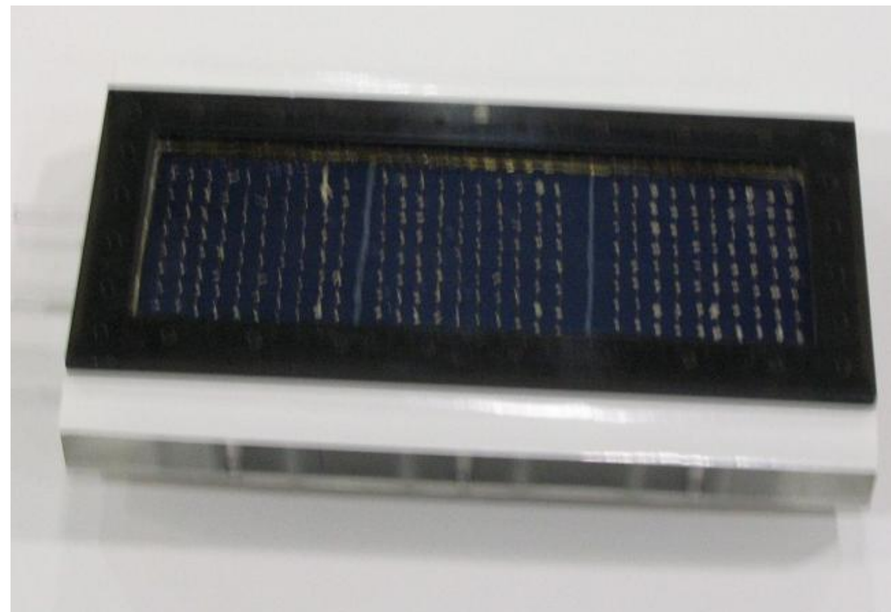
Task 4: Immersion-type PEC cell

- United Solar Ovonic Corp has supplied five sheets (~10 in by 14 in in size) of triple-junction solar cells produced from its roll-to-roll machine for use as substrate to deposit various catalyst materials for PEC application.
- Immersion-type PEC cell continued to be designed and improved.

Task 5: Fabrication of Substrate-Type PEC cells

4” x 12” substrate-type PEC cells





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Hydrogen Production Rate

Hydrogen Production			Average H2 Production
Time (min)	Volume (mL)	Amount (cc/min)	
1.250	10	8.00000	6.22932
2.167	15	6.92201	
3.183	20	6.28338	
4.130	25	6.05327	
5.030	30	5.96422	
6.230	35	5.61798	
8.183	45	5.49921	
9.100	50	5.49451	

0.82 sun intensity

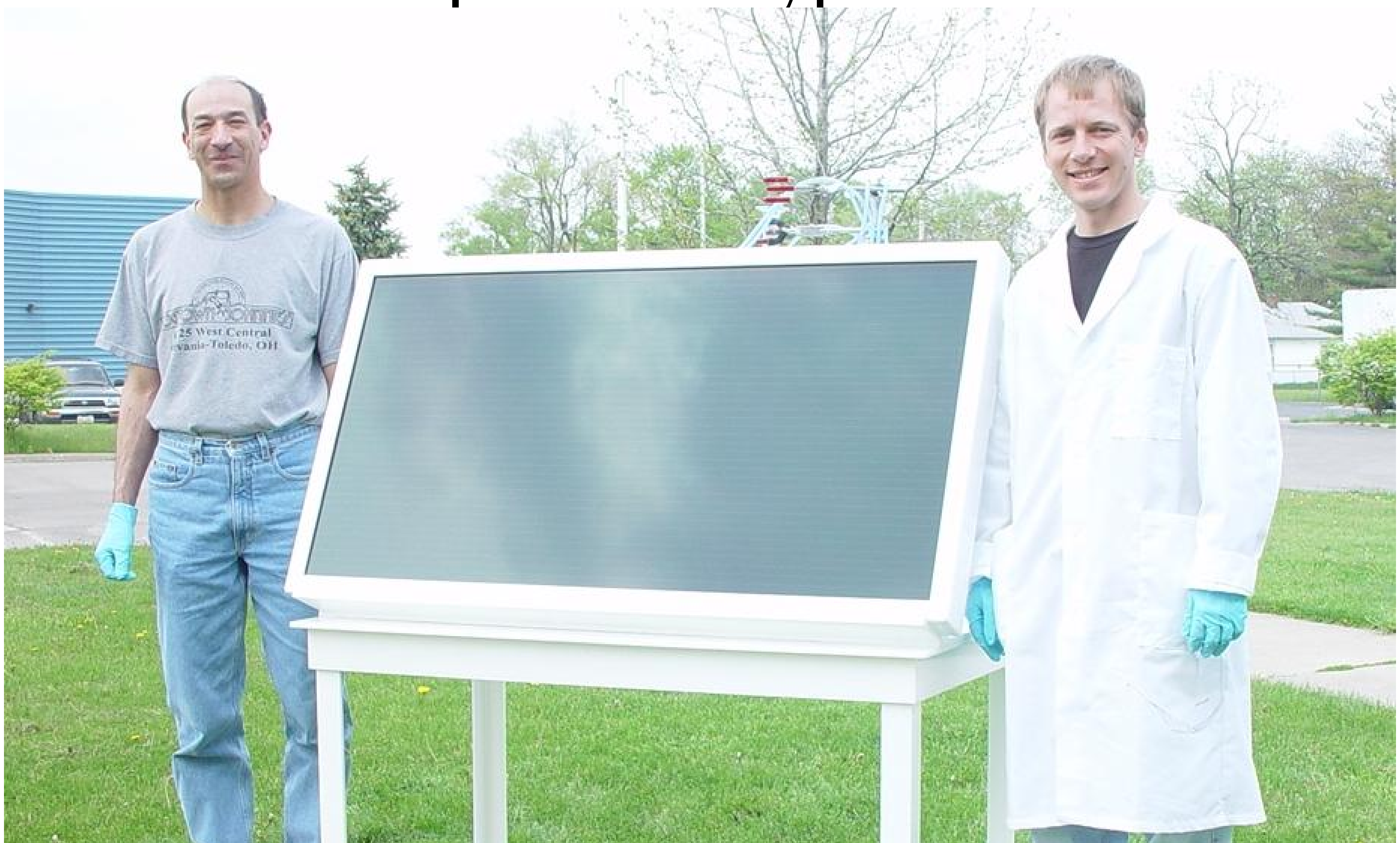
H2 production rate: 6.2 cc/min

Sample size: 4”x12”

STH Efficiency: ~5%

Other Related Studies

- Fabrication of superstrate-type of PEC cells



H_2 generate rate: 100 – 120 cc/min under 1 sun intensity.

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Mini-production of Solar Hydrogen Generation Panels

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Future Work

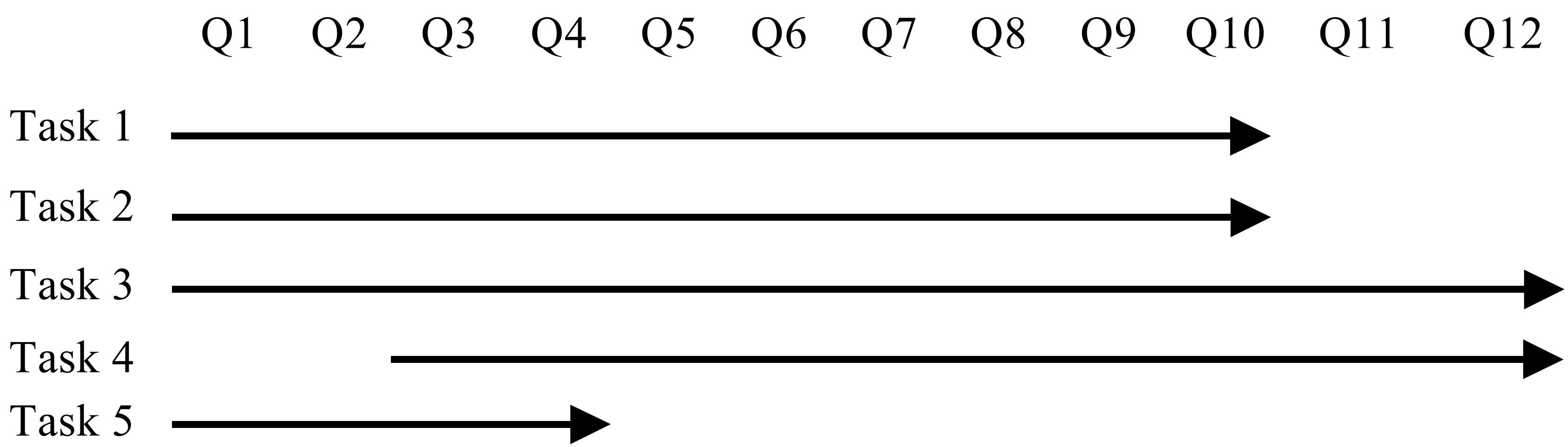
Task 1: Transparent, Conducting and Corrosion Resistant coating for triple-junction tf-Si based photoelectrode

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 $8ft^2$, substrate-type PEC panels



Publications and Presentations

- Presentation, "Sputter Deposition of Fe2O3 Films for Photoelectrochemical Hydrogen Production", 208th Meeting of the Electrochemical Society, Los Angeles, CA, October 16-21, 2005.
- J. Turner, International Partnership for Hydrogen Energy, Renewable Hydrogen Workshop, invited presentation "Photoelectrochemical Hydrogen Production", Seville, Spain, October 26, 2005.
- J. Turner, Cermae Energy Challenges Workshop, invited presentation "Hydrogen Production Methods: Water Photolysis", Barcelona, Spain, October 28, 2005
- Presentation, "Solar Generation of Hydrogen – a New Industry", University of Science and Technology of China, Hefei, China, July 3, 2005
- Presentation, "Photoelectrochemical Production of Hydrogen from Water Using SunlightInstitute of Semiconductors", Chinese Academy of Sciences, Beijing, China, July 4, 2005.

Patent Applications Filed

- Integrated Photoelectrochemical Cell and System Having a Liquid Electrolyte
  - Inventors: Xunming Deng and Liwei Xu
  - Provisional patent: Nov. 2002
  - Utility and PCT patent: Nov. 2003
  - Selection of countries: United States, Germany and Japan, May 2005

- Integrated Photoelectrochemical Cell and System Having a Solid Polymer Electrolyte
  - Inventors: Xunming Deng and Liwei Xu
  - Provisional patent: Nov. 2002
  - Utility and PCT patent: Nov. 2003
  - Selection of countries: United States, May 2005

- Integrated Photovoltaic-electrolysis cell
  - Inventors: Mahabala Adiga, Xunming Deng. Aarohi Vijh and Liwei Xu
  - Provisional patent application filed April 11, 2005
  - PCT patent application: April 10, 2006

Hydrogen Safety

The most significant hydrogen hazard associated with this project is:

- Hydrogen generated from PEC panels needs to be appropriately handled.

Our approach to deal with this hazard is:

- Follow related federal and state guidelines for handling the hydrogen generated in our PEC panels
- Install adequate ventilations
- Provide safety training to all personals handling hydrogen

Other significant hazard related to this research is the handling of hazard gases such as PH_3, GeH_4, SiH_4, BF_3, H_2 during the deposition of semiconductor layers for the photoelectrodes

- Have installed comprehensive safety measures for the handling of toxic gasses including
- toxic gas monitors probing various areas of deposition machines.
- The gas monitor can be accessed remotely and is monitored by police department.
- 24-hour training course has been provided to system operator.
- Visit by Toledo Fire department to discuss various safety issues.

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Team Members

- **Midwest Optoelectronics, LLC**

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

- **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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