

Midwest Optoelectronics



DOE Hydrogen Program

Critical Research for Cost-Effective Photoelectrochemical Production of Hydrogen

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05/19/2009

6 to 9 PM - Grand Ballroom

Project ID #

PDP_07_Ingler

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1872



NREL National Renewable Energy Laboratory

Innovation for Our Energy Future

A national laboratory of the U.S. Department of Energy
Office of Energy Efficiency & Renewable Energy



Overview

Timeline

- Project start date: 10/13/2004
- Project end date: 05/31/2010
- Percent complete: 50%

Budget

- Total project funding
 - DOE share: \$2,921,501
 - Contractor share: \$760,492
- Funding received in FY07: \$400,000, \$200,000 for NREL
- Funding received in FY08: \$500,000
- Funding received for FY09: \$0

Barriers

- DOE MYPP Objective for PEC:
 - Develop advanced renewable PEC hydrogen generation technologies.
 - By 2018, verify the feasibility of these technologies to be competitive in the long term.
- Technical Targets:
 - 2013: STH Eff > 8%; Durability >1,000 hours;
 - 2018: STH Eff > 10%; Durability >5,000 hours;
- PEC Hydrogen Generation Barriers - MYPP 3.1.4:
 - Y. Materials Efficiency
 - Z. Materials Durability
 - AA. PEC Device and System Auxiliary Material
 - AC. Device Configuration Designs
 - AD. Systems Design and Evaluation

Partners

- Xunlight Corporation
 - Dr. Anke Abken
- University of Toledo
 - Dr. William B. Ingler Jr.
- National Renewable Energy Lab.
 - Dr. John Turner

Project Objectives (Relevance)

- **To develop critical technologies required for cost-effective production of hydrogen from sunlight and water using thin film-Si based photoelectrodes.**
- **Two approaches are taken for the development of efficient and durable photo-electrochemical cells.**
 - **An immersion-type photoelectrochemical cell in which the photoelectrode is immersed in electrolyte.**
 - **A substrate-type photoelectrochemical cell in which the photoelectrode is not in direct contact with electrolyte.**

Milestones (Approach)

Year 1:

- *Identify materials that meet the performance criteria for transparent, conducting, corrosion-resistant (TCCR) materials, including having stability for up to 300 hours. First round of materials to be produced at 350°C or lower with 70% or greater transparency and at least 3 mA/cm² photocurrent.*
- *Identify materials that meet the performance criteria for photoactive semiconductor (PAS) materials, including having stability for up to 300 hours. First round of materials to be produced at 350°C or lower with 70% or greater transparency and at least 3 mA/cm² photocurrent.*

Year 2:

- *Develop TCCR material with a stability up to 700 hours. Second round of materials to be produced at 300°C or lower with 85% or greater transparency and at least 5 mA/cm² photocurrent.*
- *Develop high-quality PAS material with a stability up to 700 hours. Second round of materials to be produced at 300°C or lower and at least 5 mA/cm² conductivity.*
- *Go/No-Go Decision Point (this decision point will occur at the end of Year 2 and will coincide with the end of Budget Period 1): Go/no go decision will be based, in part, on progress toward developing TCCR and PAS materials capable of meeting the following performance criteria: ≥700 hours of stability, capable of being fabricated at ≤300°C, ≥85% or greater transparency, and ≥5 mA/cm² photocurrent (TCCR material); ≥700 hours of stability, capable of being fabricated at ≤300°C, and ≥5 mA/cm² photocurrent (TCCR material).*

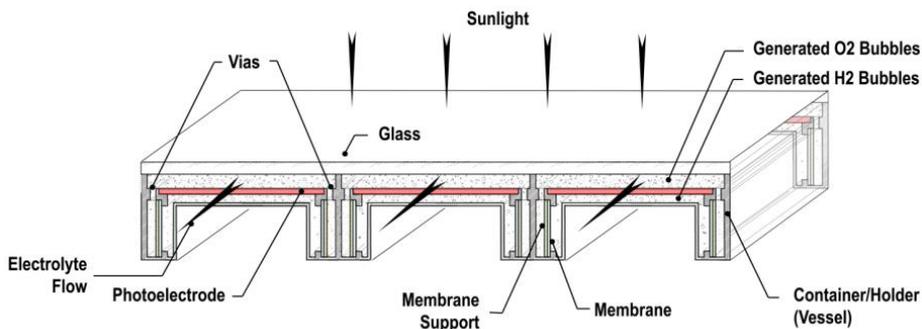
Year 3:

- *Develop TCCR material with stability up to 1,000 hours. Second round of materials to be produced at 250°C or lower with 90% or greater transparency and at least 8 mA/cm² photocurrent.*
- *Develop high-quality PAS material with stability up to 1,000 hours. Second round of materials to be produced at 250°C or lower and at least 8 mA/cm² photocurrent.*
- *Complete techno-economic analysis and energy analysis for the PEC systems for hydrogen production.*

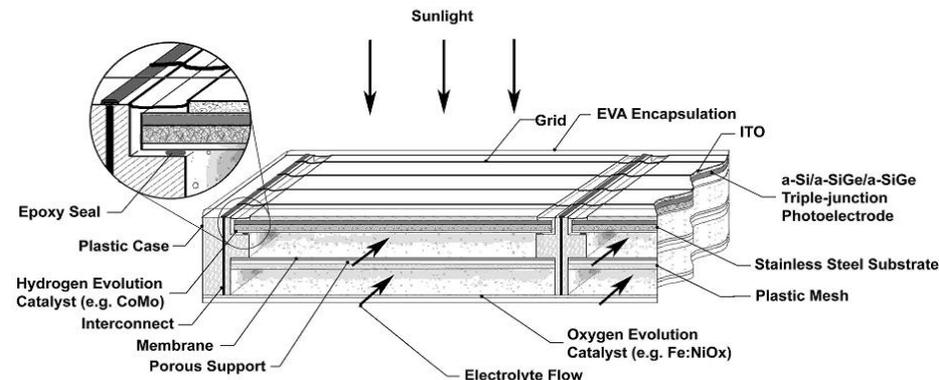
Approach

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

An immersion-type PEC cell



A substrate-type PEC cell

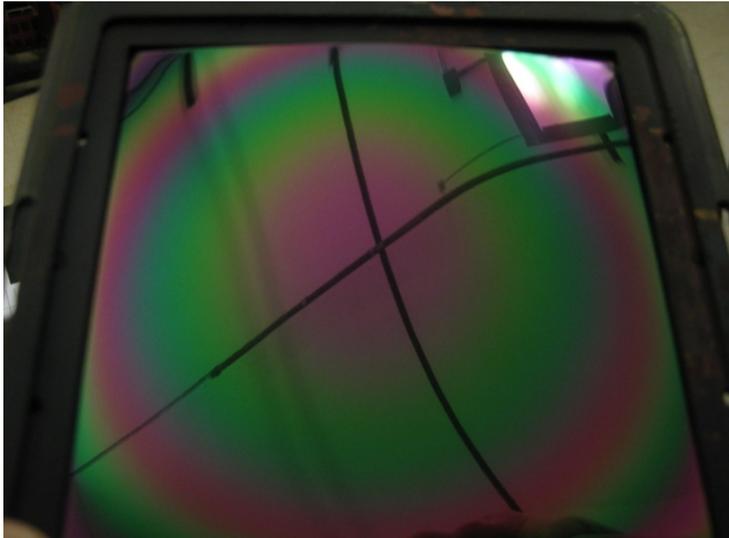


Research Tasks (Approach)

- **Task 1:** Transparent, conducting and corrosion resistant coating for triple-junction tf-Si based photoelectrode;
[Phase 1: 100%; Phase 2: 50%; Total: 50%]
- **Task 2:** Hybrid multijunction PEC electrode having semiconductor-electrolyte junction;
[Phase 1: 100%; Phase 2: 50%; Total: 50%]
- **Task 3:** Understanding and characterization of photoelectrochemistry;
[Phase 1: 100%; Phase 2: 50%; Total: 50%]
- **Task 4:** Development of device designs for low-cost, durable and efficient immersion-type PEC cells and systems;
[Phase 1: 100%; Phase 2: 50%; Total: 50%]
- **Task 5:** Development of device designs for large-area, substrate-type PEC panels;
[Phase 1: 100%; Phase 2: 50%; Total: 50%]

Technical Accomplishments - Task 1

- Study of $\text{In}_2\text{O}_3\text{-Fe}_2\text{O}_3$ as a TCCR material.
- Research has focused on maximizing the long-term stability and current density of the film while maximizing transparency.
- The best sample so far was made at 275°C , 100 W Fe_2O_3 and 30 W In in 6% oxygen gas for two hours of deposition, and had an increasing current density of 4.32 mA/cm^2 at 1.6 V after 28 cycles.
- This was part of a relatively small region of stability in the parameter space including temperatures from 250°C to 275°C and oxygen concentrations from 5% to 6%.



- Stable current density appears to peak for total flow of around 11 sccm during deposition, at least for samples made at 250°C .
- Current study on $\text{In}_2\text{O}_3\text{-InFe}_2\text{O}_4$.
- Optimized conditions being used for deposition on $4'' \times 4''$ substrates.

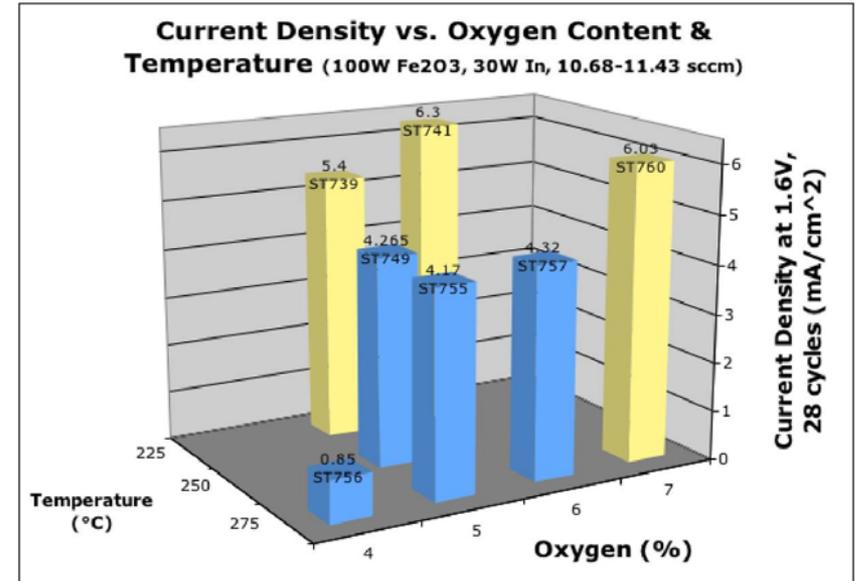
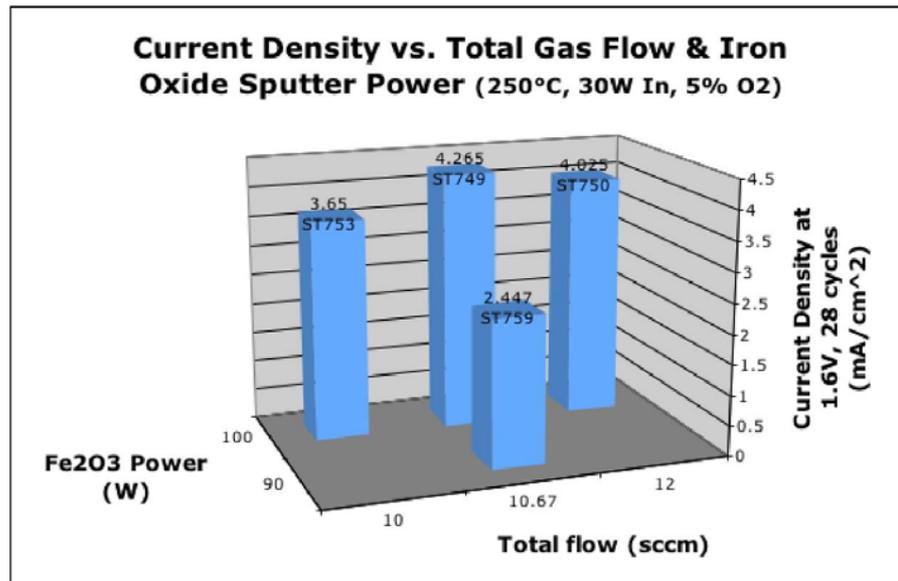
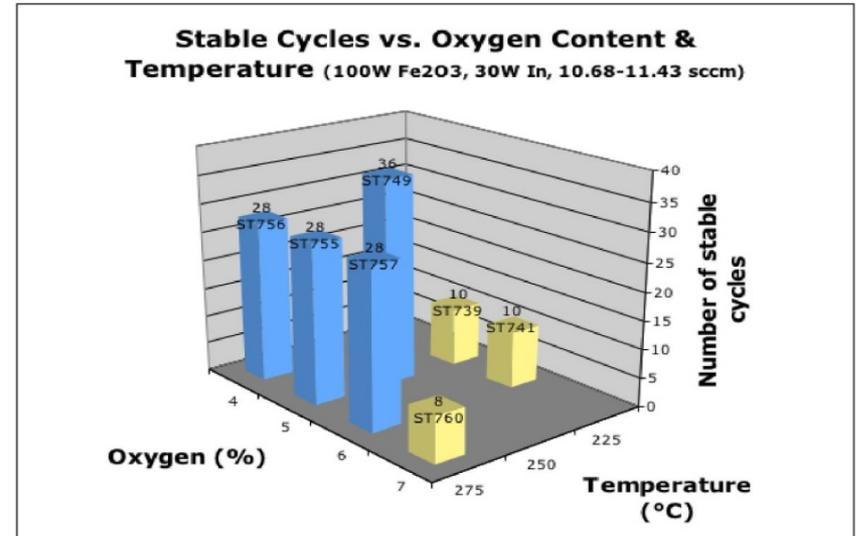
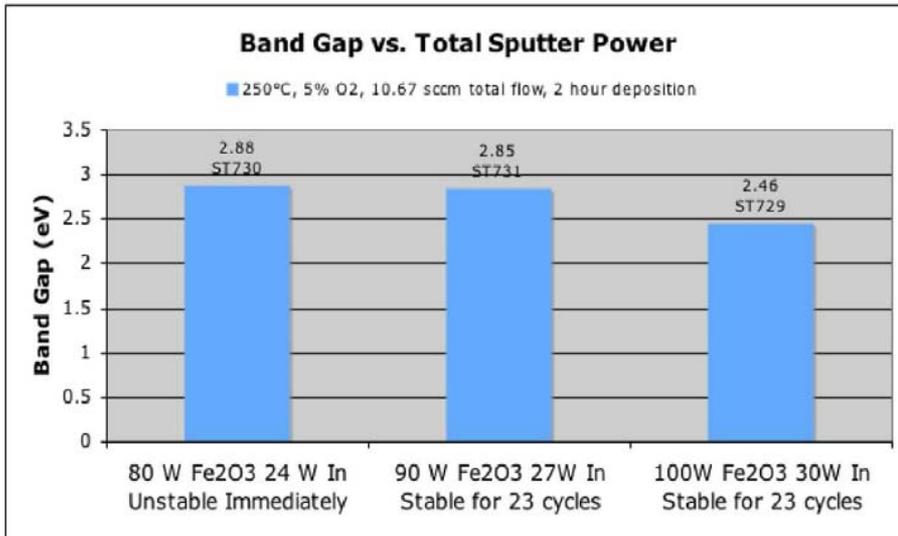
$\text{In}_2\text{O}_3\text{-Fe}_2\text{O}_3$ TCCR

Technical Accomplishments - Task 1

- Experimental data and deposition parameters of samples deposited onto TEC-15 (SnO₂:F) glass, with data from cyclic voltammetry and UV-Vis spectrophotometry. 'S' denotes stable, 'U' denotes unstable. Samples marked with a star (*) were made with a new iron oxide target.

Sample	Temp (°C)	In (W)	Fe ₂ O ₃ (W)	Ar (sccm)	Ar/O ₂ (sccm)	O ₂ (%)	Total Flow (sccm)	Dep. Time	Stability	Stable Cycles	1st cycle (mA/cm ²)	28 cycles (mA/cm ²)	Eg (eV)
729	250	30	100	8.0	2.67	5.005%	10.67	2:00	S	23	8.2	4.58	2.4554
730	250	24	80	8.0	2.67	5.005%	10.67	2:00	U	0	11.3	3.7	2.8818
731	250	27	90	8.0	2.67	5.005%	10.67	2:00	S	23	6.64	6.47	2.8492
732	250	30	100	8.0	3.43	6.002%	11.43	2:00	U	0	7.12	-	
733	250	30	100	10.8	2.70	4.000%	13.50	2:00	S	26	4.7	6	2.4538
734	250	30	100	8.0	2.67	5.005%	10.67	2:00	S	28	0.8	-	
737	200	30	100	8.0	3.43	6.002%	11.43	2:00	U	0	7.5	-	2.7985
739	225	30	100	8.0	2.67	5.005%	10.67	2:00	S	10	8.52	5.4	2.8102
741*	225	30	100	8.0	3.43	6.002%	11.43	2:00	S	10	7.3	6.3	
743*	225	30	100	9.1	3.90	6.000%	13.00	2:00	U	0	13.05	-	
744*	225	30	20-100	8.0	2.67	5.005%	10.67	2:00	U	0	12.2	-	
746*	200	30	100	8.0	3.43	6.002%	11.43	2:00	U	0	16.5	-	
748*	225	30	130	8.0	3.43	6.002%	11.43	1:00	U	0	11.5	-	
749*	250	30	100	8.0	2.67	5.005%	10.67	2:00	S	36	5.2	4.265	
750*	250	30	100	9.0	3.00	5.000%	12.00	2:00	S	28	6	4.025	
753*	250	30	100	7.5	2.50	5.000%	10.00	2:00	S	28	6.8	3.65	
755*	275	30	100	8.0	2.67	5.005%	10.67	2:00	S	28	6.1	4.17	
756*	275	30	100	8.8	2.20	4.000%	11.00	2:05	S	28	1.49	0.85	
757*	275	30	100	7.7	3.30	6.000%	11.00	2:00	S	28	5.7	4.32	
758*	250	30	100	8.0	2.67	5.005%	10.67	2:01	S	28	3.85	1.8	
759*	250	30	90	8.0	2.67	5.005%	10.67	2:00	S	28	4.74	2.447	
760*	275	30	100	7.2	3.88	7.004%	11.08	2:00	S	8	9.33	6.03	

Technical Accomplishments - Task 1

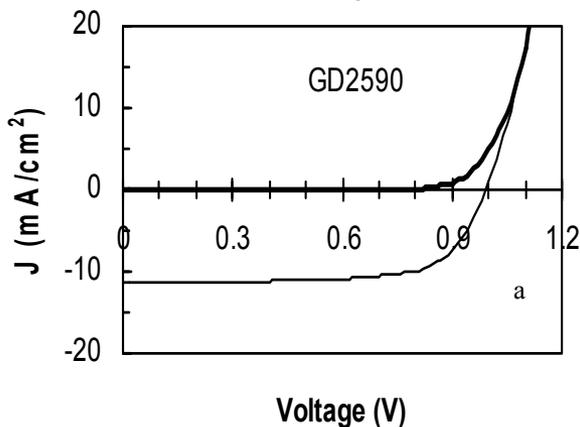


Technical Accomplishments - Task 2

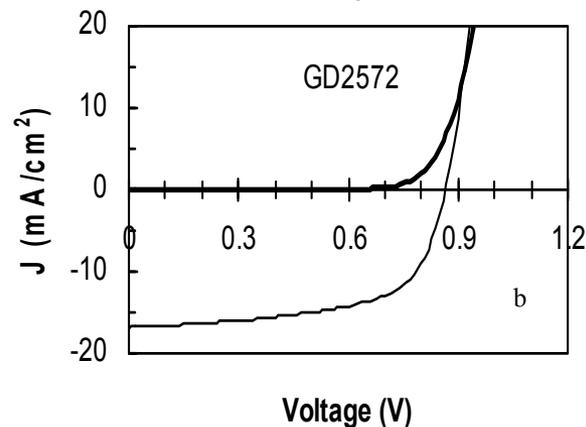
- Fabrication of triple-junction a-Si/a-SiGe/a-SiGe solar cells (Photoelectrodes)
- Fabrication of triple-junction a-Si/a-SiGe/nc-Si solar cells (Photoelectrodes)
- Effect of $\text{GeH}_4/\text{Si}_2\text{H}_6$ flow ratio effect on the performance of a-SiGe solar cells was studied.
- I-V curves of a-SiGe solar cells deposited with various $\text{GeH}_4/\text{Si}_2\text{H}_6$ flow ratios are shown:

Sample No.	$\text{GeH}_4/\text{Si}_2\text{H}_6$ Flow ratio	V_{oc} (V)	J_{sc} (I-V)	FF (%)	EFF (%)
GD2590	0	0.99	11.34	70.14	7.89
GD2593	0.8	0.90	14.97	59.24	7.95
GD2572	1.1	0.87	16.95	61.26	9.05
GD2571	1.35	0.83	17.01	60.94	8.62
GD2560	2	0.78	18.19	58.53	8.35

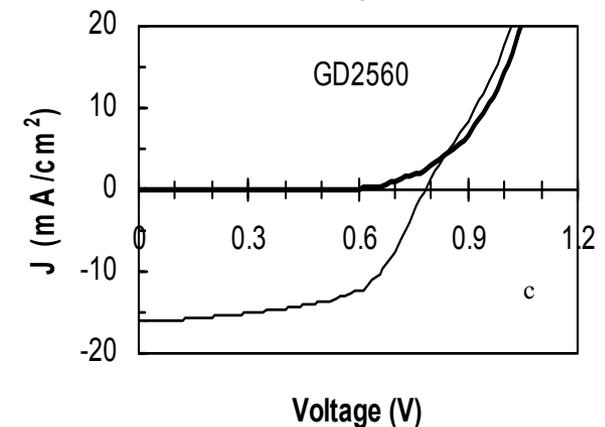
$\text{GeH}_4/\text{Si}_2\text{H}_6$ ratio: 0



$\text{GeH}_4/\text{Si}_2\text{H}_6$ ratio: 1.1



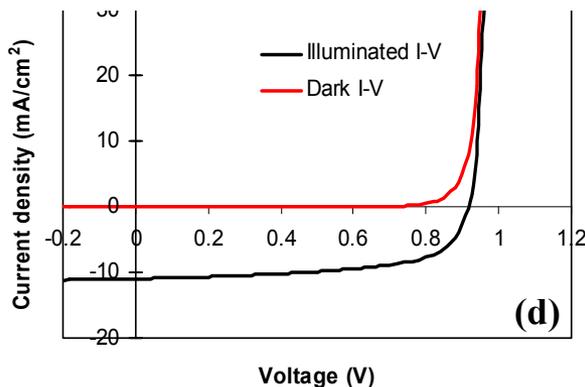
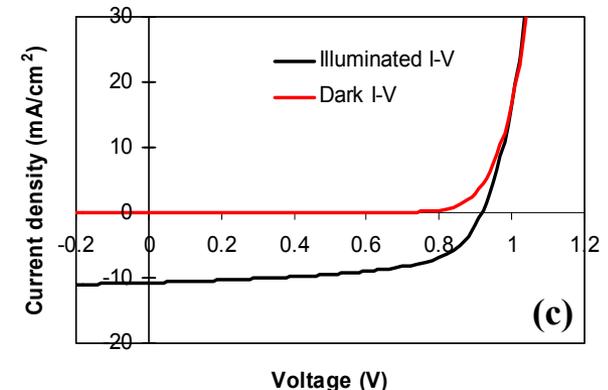
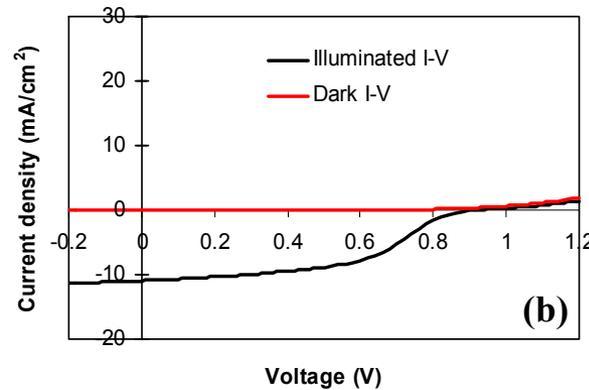
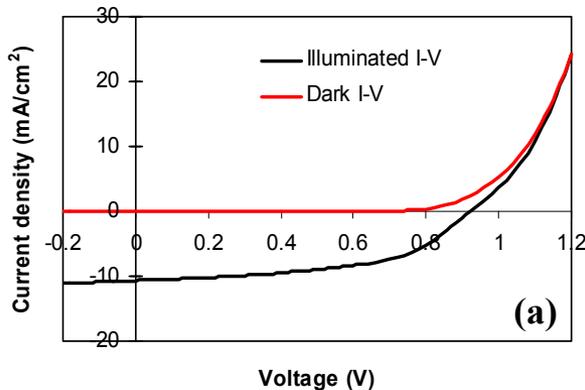
$\text{GeH}_4/\text{Si}_2\text{H}_6$ ratio: 2.0



Technical Accomplishments - Task 2

- The effect of different plasma treatments on the photovoltaic parameters of a-Si solar cells on SS substrates was studied;

Sample No	V_{oc} (V)	J_{sc} (mA/cm ²)	FF (%)	Eff (%)	plasma
3mw176(A)	0.924	11.004	53.459	5.433	No any
3mw179(B)	0.924	11.179	45.845	4.738	Ar + O
3mw181(C)	0.925	10.703	59.608	5.904	Ar
3mw182(D)	0.919	10.881	63,301	6.332	H



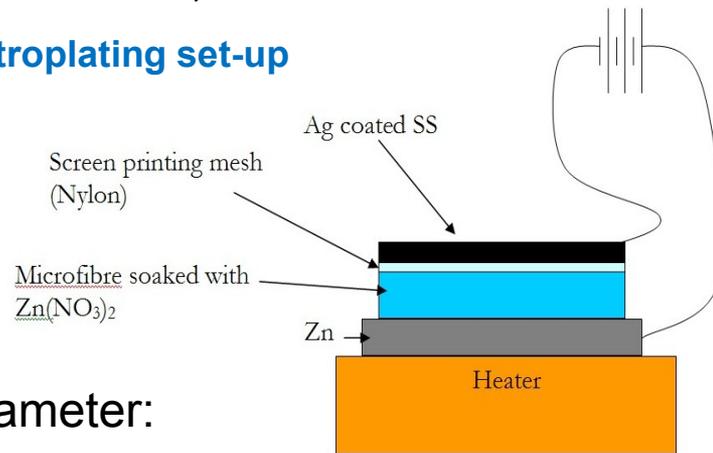
The IV-curves show the effect of plasma pretreatment on the I-V curves of a-Si solar cells deposited on stainless steel substrates;

- (a) without any plasma treatment,
- (b) with Ar (95%) + O (5%) plasma,
- (c) with Ar (100%) plasma, and
- (d) with H (100%) plasma treatment.

Technical Accomplishments - Task 4

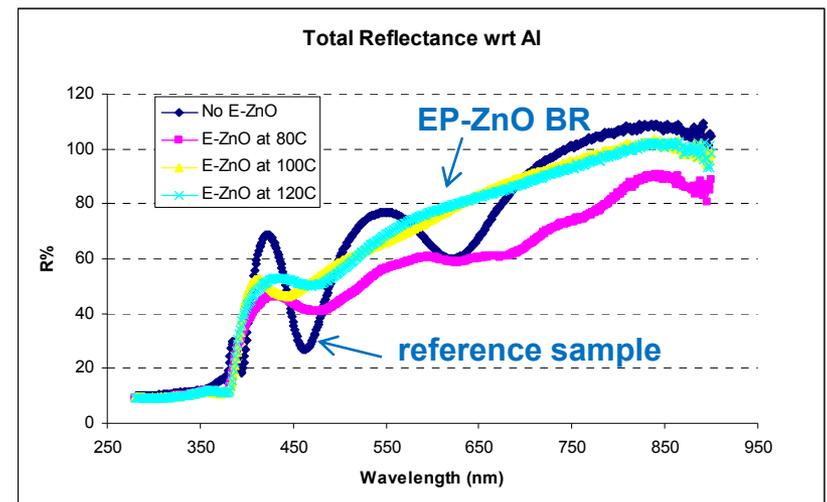
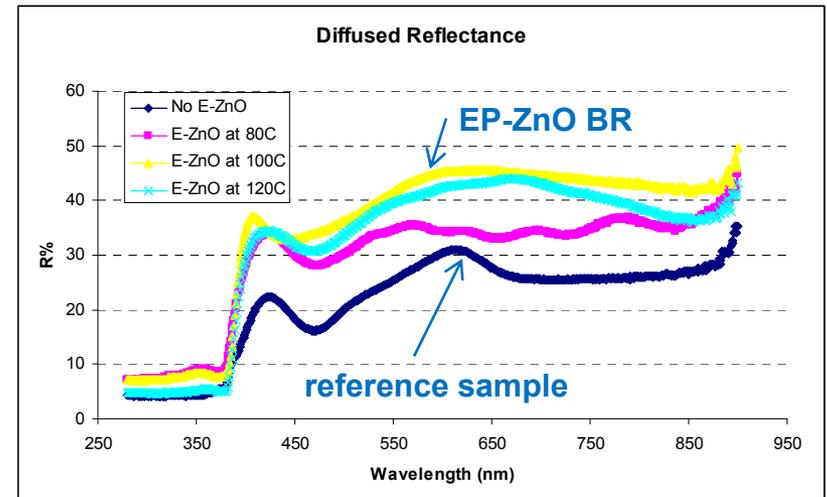
- The effect of electroplating parameters on ZnO back reflector coatings was studied;

Electroplating set-up



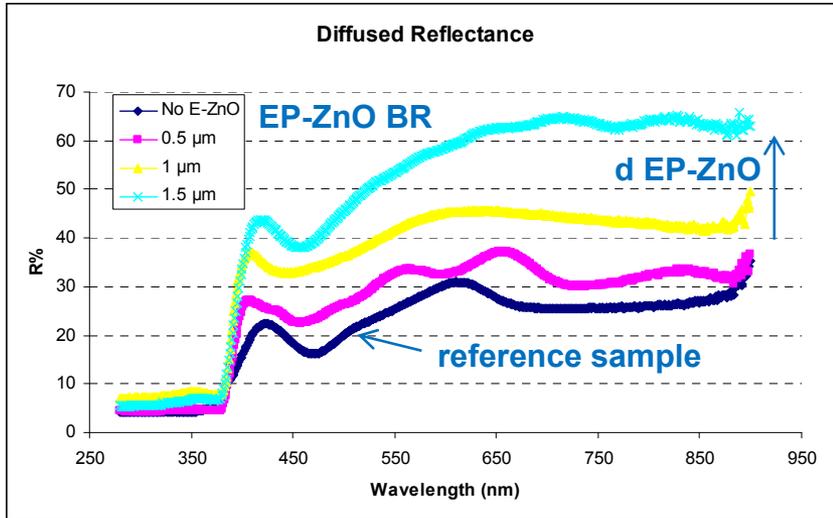
- Parameter:
 - Temperature
 - Nylon Mesh
 - ZnO Thickness
- The total and diffused reflectance of electroplated ZnO layer deposited at different deposition temperatures was measured.
- The blue curves show a reference sample with sputtered ZnO/Ag layer.

Optical Reflectance of electroplated ZnO back reflector

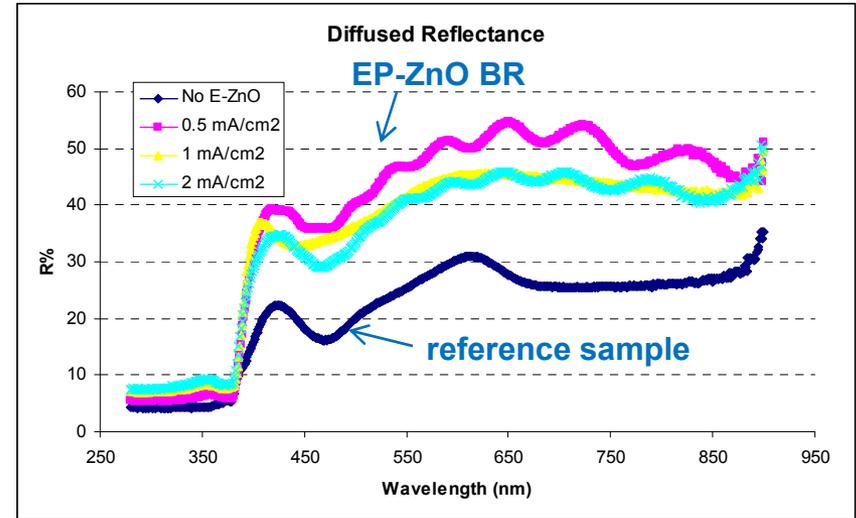


Technical Accomplishments - Task 4

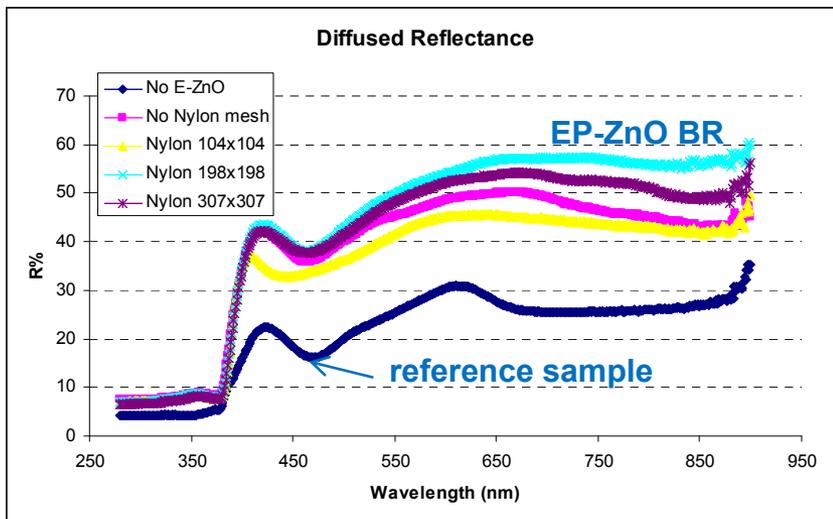
Diffused reflectance: thickness variation of ZnO layer



Diffused reflectance: variation of current density



Diffused reflectance: different Nylon mesh

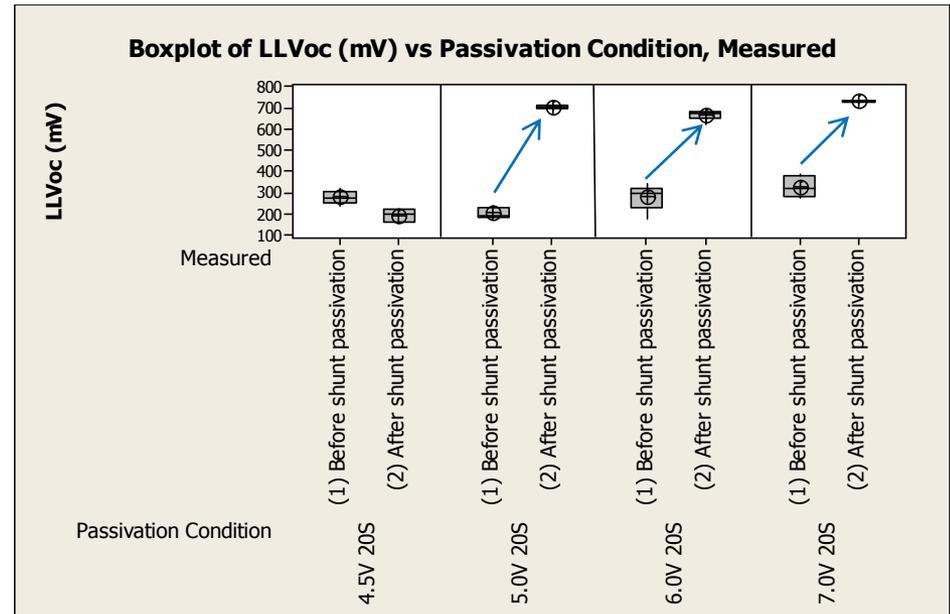


- The graphs show the effect of different processing parameter (current density, Nylon mesh) and the impact of EP-ZnO layer thickness on diffused reflectance;
- Increasing the EP-ZnO thickness increases the diffused reflectance and surface roughness;

Technical Accomplishments - Task 5

- Work on developing photoassisted electrochemical process for shunt passivation focuses on metal salt selection used as electrolyte.
- Metal salt A was previously used for shunt passivation of PEC devices (no back reflector). Passivating with salt A requires using a low pH of the electrolyte, which might lead to corrosion when back reflectors (Al/Ag/ZnO layer stacks) are used.
- As an alternative metal salt B was tested. The low light open circuit voltage (LLV_{OC}) improves for passivation conditions using 5-7V for 20 sec.
- Work on shunt passivation using metal salt B,C for samples with back reflectors from Xunlight's 2 MW roll-to-roll (RTR) system is in progress. Salt B,C contain the same metal cation but a different anion; they are less corrosive than salt A and allow environmental friendly disposal. Although promising results for salt B have been achieved it is not as effective as using salt A.

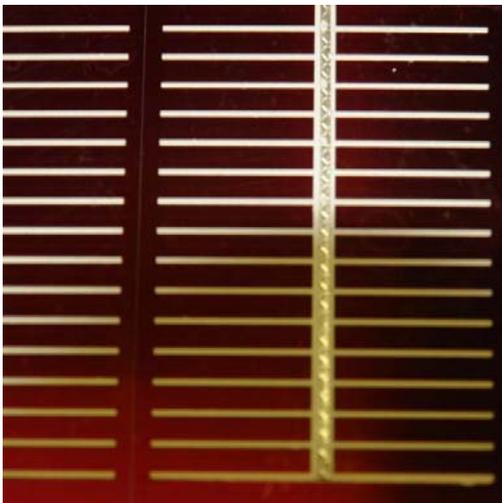
Low light V_{OC} measurement: metal salt B as electrolyte



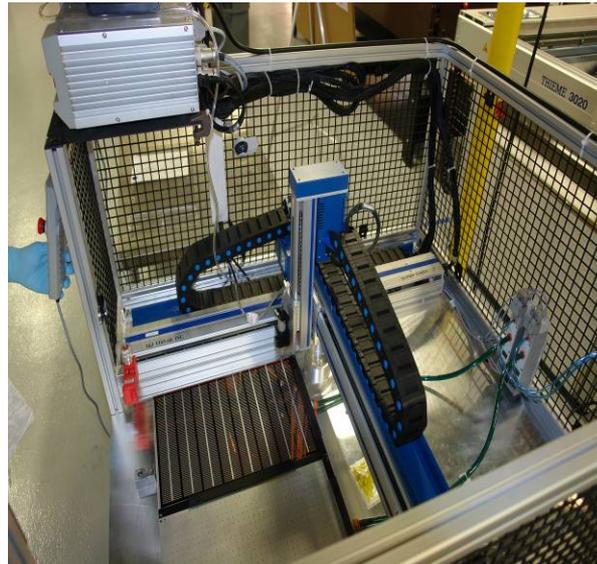
Technical Accomplishments - Task 5

- A method for ink-dot application was developed; the method will support lead to reliability improvements of substrate-type PEC cells.
- A method for increasing the durability of the metal foil adhesion to the silver current collection grid was developed. The robot is used to apply ink dots, or “tabbing”, along a central metal foil conductor.
- The following procedure was used for the ink-dot application:
 - The operator will load a single 11” × 17” PV cell into the robot and engage a vacuum hold-down plate mechanism. The robot dispenser arm will be aligned to the start and stop points.

Device after ink dot application



Fisnar ink tabbing robot



- Then, all ink application points in between are calculated and the program runs accordingly.
- After the robot tabber runs its program the ink tabbing is cured in a conveyor oven.

Collaborations

Partners:

- NREL (Federal):
NREL is working on improved understanding of PEC process for a-Si based photoelectrodes (in collaboration with Dr. John Turner).
- University of Toledo (Academic):
UT is developing TCCR coatings, H₂ catalysts for immersion and substrate-type PEC cells. Developing prototype 1ft × 1ft PEC devices with UT.

Technology Transfer:

- NREL:
NREL is supporting with device measurements on a-Si, a-SiGe, etc. solar cells (device characterization, stability testing etc.).
- University of Toledo:
UT is integral as they finished another DOE H₂ grant that was on basic research transferred to this project. UT is continuing development of the material work they started on the previous grant.

Proposed Future Work

- Task 1: Continue study and optimization of In_2O_3 - InFe_2O_4 TCCR coatings on solar cell surfaces.
- Task 2: Develop chemical plating for II/VI-semiconductors (CdS) as PAS & TCCR coating for immersion-type hybrid PEC cells.
- Task 4: Supported by University of Toledo 4" × 4" immersion-type PEC cells will be developed.
- Task 5: Supported by University of Toledo a 1ft × 1ft substrate-type PEC cell will be developed.
 - Long-term reliability studies and measurements will be done.
- Task 5: The shunt passivation process will be improved focusing on salt studies used as electrolytes.

Project Summary

- **Relevance:** Addresses DOE program objectives, specifically high-efficiency and low-cost production of hydrogen using photoelectrochemical methods.
- **Approach:** An immersion-type photoelectrochemical cell where the photo-electrode is immersed in electrolyte and a substrate-type photo-electrochemical cell where the photoelectrode is not in direct contact with electrolyte.
- **Technical Accomplishments and Progress:**
 - Demonstrated a 4" × 12" substrate-type PEC cell with 12" × 12" model under development.
 - Have secured external funding for development of roll-to-roll unit for a-Si solar cell deposition at Xunlight.
- **Technology Transfer/Collaborations:**
 - Active collaboration with UT towards commercialization of research done at MWOE and Xunlight.
- **Proposed Future Research:**
 - Will leverage research done at UT to develop substrate-type PEC. Computational components at UT and NREL will be used for improved identification of material classes for sputter deposition of PAS and TCCR layers.