

# Critical Research for Cost-effective Photoelectrochemical Production of Hydrogen

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This presentation does not contain any proprietary or confidential information

Project ID #  
170-PDP-35



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: 10/12/2007
- Percent complete: 1%

## Budget

- Total project funding
  - DOE share: \$2,921,501
  - Contractor share: \$760,492
- Funding received in FY04 to date : 0
- Funding for FY05: ?

# 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

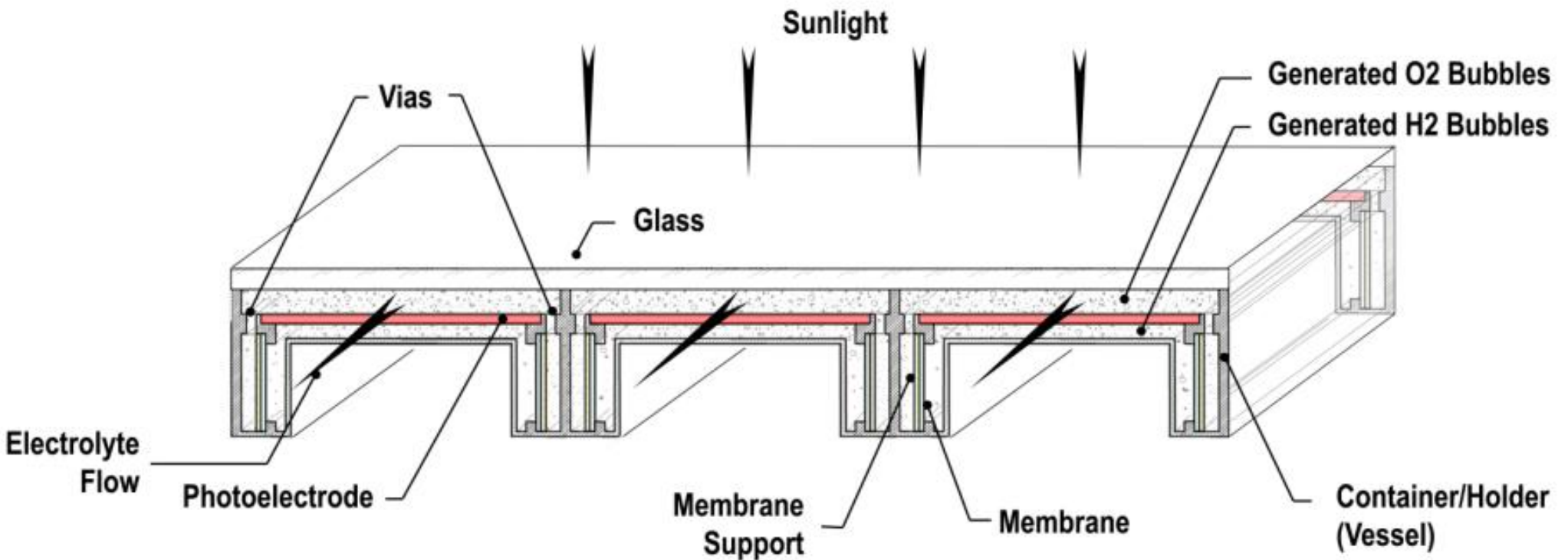
## Partners

- University of Toledo
- National Renewable Energy Laboratory
- United Solar Ovonic Corp.

# 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, immersion-type 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.

# Approach - PEC cell

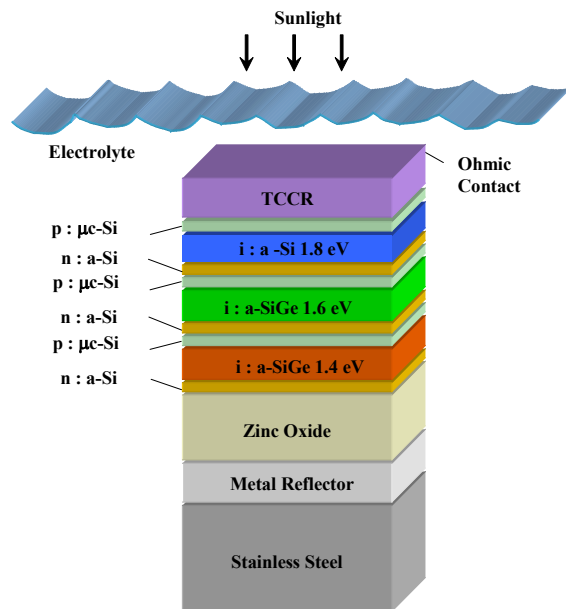


# Approach - PEC electrode

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

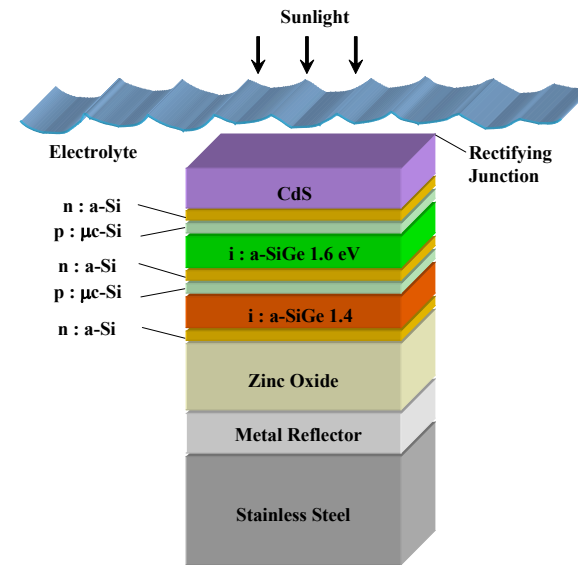
## Approach 1 (Task 1):

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



## Approach 2 (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



# Approach - 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 8ft<sup>2</sup>, substrate-type PEC panels

## Progress/Results

# DC Magnetron Sputter Deposition of $\text{TiO}_2$ , $\text{Fe}_2\text{O}_3$ and $\text{WO}_3$

- Completed the construction of two new sputter deposition chambers for oxides depositions, with each chamber having three sputter targets capable of depositing from three different sources simultaneously
- Deposited  $\text{TiO}_2$ ,  $\text{Fe}_2\text{O}_3$  and  $\text{WO}_3$  films.
- For  $\text{TiO}_2$ , deposited films with
  - different oxygen content
  - different nitrogen doping
  - different indium doping

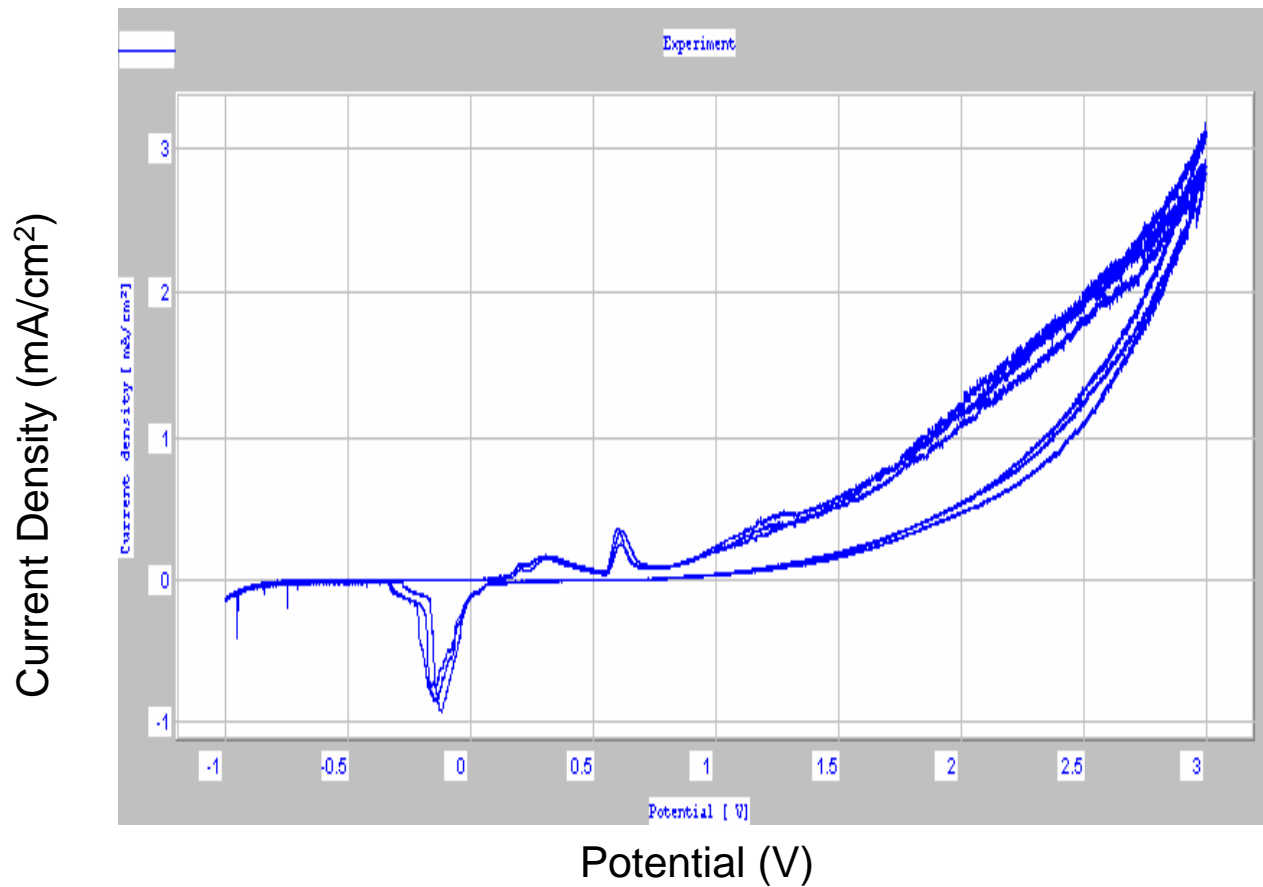
# Deposition Conditions for TiO<sub>2</sub> films

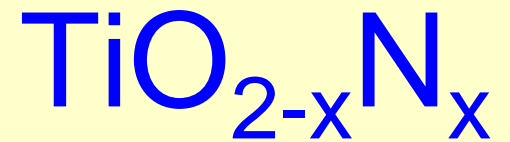
| Sample | Power<br>(W) | Time<br>(min) | Temp<br>(°C) | Pressure<br>(mTorr) | Atmosphere             | Comments |
|--------|--------------|---------------|--------------|---------------------|------------------------|----------|
| ST005  | 50           | 60            | 200          | 4                   | Ar                     | NONE     |
| ST006  | 50           | 60            | 250          | 4                   | Ar                     | NONE     |
| ST007  | 50           | 60            | 300          | 4                   | Ar                     | NONE     |
| ST008  | 50           | 60            | 150          | 4                   | Ar                     | NONE     |
| ST009  | 40           | 100           | 200          | 4                   | Ar                     | NONE     |
| ST010  | 40           | 100           | 250          | 4                   | Ar                     | NONE     |
| ST011  | 40           | 100           | 300          | 4                   | Ar                     | NONE     |
| ST012  | 40           | 100           | 150          | 4                   | Ar                     | NONE     |
| ST013  | 60           | 60            | 200          | 4                   | 2% O <sub>2</sub> , Ar | NONE     |
| ST014  | 60           | 60            | 250          | 4                   | 2% O <sub>2</sub> , Ar | NONE     |
| ST015  | 50           | 80            | 200          | 4                   | 2% O <sub>2</sub> , Ar | NONE     |
| ST016  | 40           | 100           | 200          | 4                   | 2% O <sub>2</sub> , Ar | NONE     |
| ST017  | 60           | 180           | 200          | 4                   | 2% O <sub>2</sub> , Ar | NONE     |
| ST018  | 30           | 120           | 200          | 4                   | 2% O <sub>2</sub> , Ar | NONE     |
| ST019  | 40           | 100           | 250          | 4                   | 2% O <sub>2</sub> , Ar | NONE     |
| ST020  | 50           | 80            | 250          | 4                   | 2% O <sub>2</sub> , Ar | NONE     |
| ST021  | 60           | 200           | 200          | 4                   | 2% O <sub>2</sub> , Ar | NONE     |
| ST022  | 40           | 100           | 150          | 4                   | 2% O <sub>2</sub> , Ar | NONE     |
| ST023  | 50           | 80            | 150          | 4                   | 2% O <sub>2</sub> , Ar | NONE     |
| ST024  | 40           | 300           | 200          | 4                   | 2% O <sub>2</sub> , Ar | NONE     |
| ST025  | 40           | 120           | 200          | 4                   | 5% O <sub>2</sub> , Ar | NONE     |
| ST026  | 40           | 120           | 250          | 4                   | 5% O <sub>2</sub> , Ar | NONE     |
| ST027  | 50           | 120           | 200          | 4                   | 5% O <sub>2</sub> , Ar | NONE     |
| ST028  | 50           | 120           | 250          | 4                   | 5% O <sub>2</sub> , Ar | NONE     |

| Sample | Power<br>(W) | Time<br>(min) | Temp<br>(°C) | Pressure<br>(mTorr) | Atmosphere                   | Comments  |
|--------|--------------|---------------|--------------|---------------------|------------------------------|-----------|
| ST029  | 60           | 120           | 200          | 4                   | 5% O <sub>2</sub> , Ar       | NONE      |
| ST030  | 60           | 120           | 250          | 4                   | 5% O <sub>2</sub> , Ar       | NONE      |
| ST031  | 60           | 180           | 200          | 2                   | 5% N <sub>2</sub> Ar         | NONE      |
| ST032  | 70           | 180           | 200          | 2                   | 5% N <sub>2</sub> Ar         | NONE      |
| ST033  | 80           | 60            | 200          | 4                   | 5% N <sub>2</sub> Ar         | NONE      |
| ST035  | 90           | 60            | 200          | 4                   | 5% N <sub>2</sub> Ar         | NONE      |
| ST042  | 80           | 60            | 200          | 4                   | 2% O <sub>2</sub> , Ar       | In, 10 W  |
| ST043  | 90           | 60            | 200          | 4                   | 2% O <sub>2</sub> , Ar       | In, 10 W  |
| ST045  | 90           | 60            | 200          | 4                   | 2% O <sub>2</sub> , Ar       | In, 15 W  |
| ST046  | 90           | 60            | 200          | 4                   | 2% O <sub>2</sub> , Ar       | In, 20 W  |
| ST047  | 80           | 60            | 200          | 4                   | 30% N <sub>2</sub> Ar        | NONE      |
| ST048  | 90           | 60            | 200          | 4                   | 30% N <sub>2</sub> Ar        | NONE      |
| ST049  | 80           | 60            | 250          | 4                   | 30% N <sub>2</sub> Ar        | NONE      |
| ST050  | 90           | 60            | 250          | 4                   | 30% N <sub>2</sub> Ar        | NONE      |
| ST051  | 100          | 60            | 200          | 4                   | 30% N <sub>2</sub> Ar        | NONE      |
| ST052  | 100          | 60            | 200          | 4                   | 2% O <sub>2</sub> , Ar       | In, 15 W  |
| ST053  | 100          | 60            | 200          | 4                   | 2% O <sub>2</sub> , Ar       | In, 20 W  |
| ST054  | 100          | 60            | 200          | 4                   | 2% O <sub>2</sub> , Ar       | In, 10 W  |
| ST056  | 100          | 60            | 200          | 4                   | 2% O <sub>2</sub> , Ar       | In, 7 W   |
| ST057  | 100          | 120           | 200          | 4                   | 2% O <sub>2</sub> , Ar       | In, 15 W  |
| ST059  | 100          | 120           | 250          | 4                   | 2% O <sub>2</sub> , Ar       | In, 15 W  |
| ST060  | 100          | 120           | 250          | 4                   | Ar/N <sub>2</sub> : 8/5 sccm | NONE      |
| ST062  | 100          | 120           | 250          | 4                   | Ar/N <sub>2</sub> : 8/5 sccm | 4h anneal |

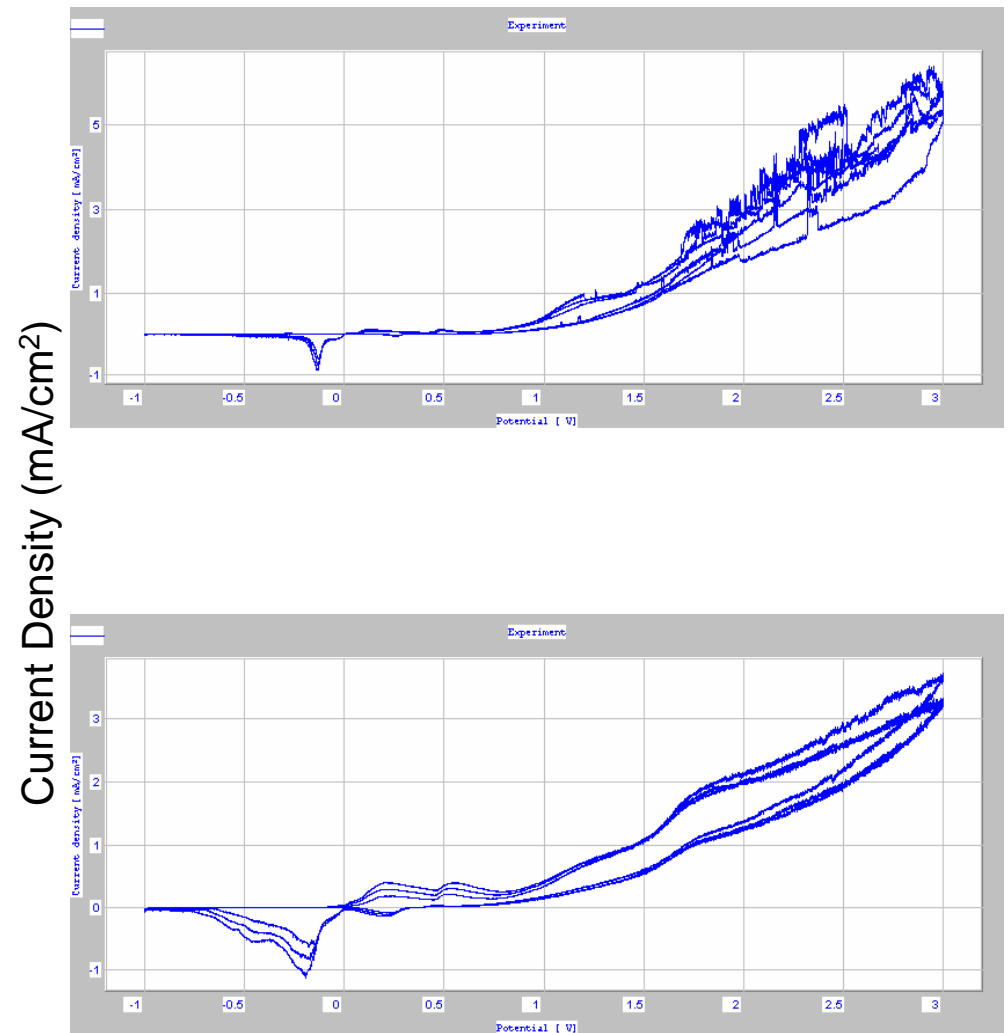
# TiO<sub>2</sub>

- I-V curve for TiO<sub>2</sub> shown in figure.
- Addition of small amounts of O<sub>2</sub> during TiO<sub>2</sub> deposition improves film's electrochemical stability





- (Top) Shows higher current density with no annealing, but still stable
- (Bottom) Annealing for 4 hrs, the film remained stable

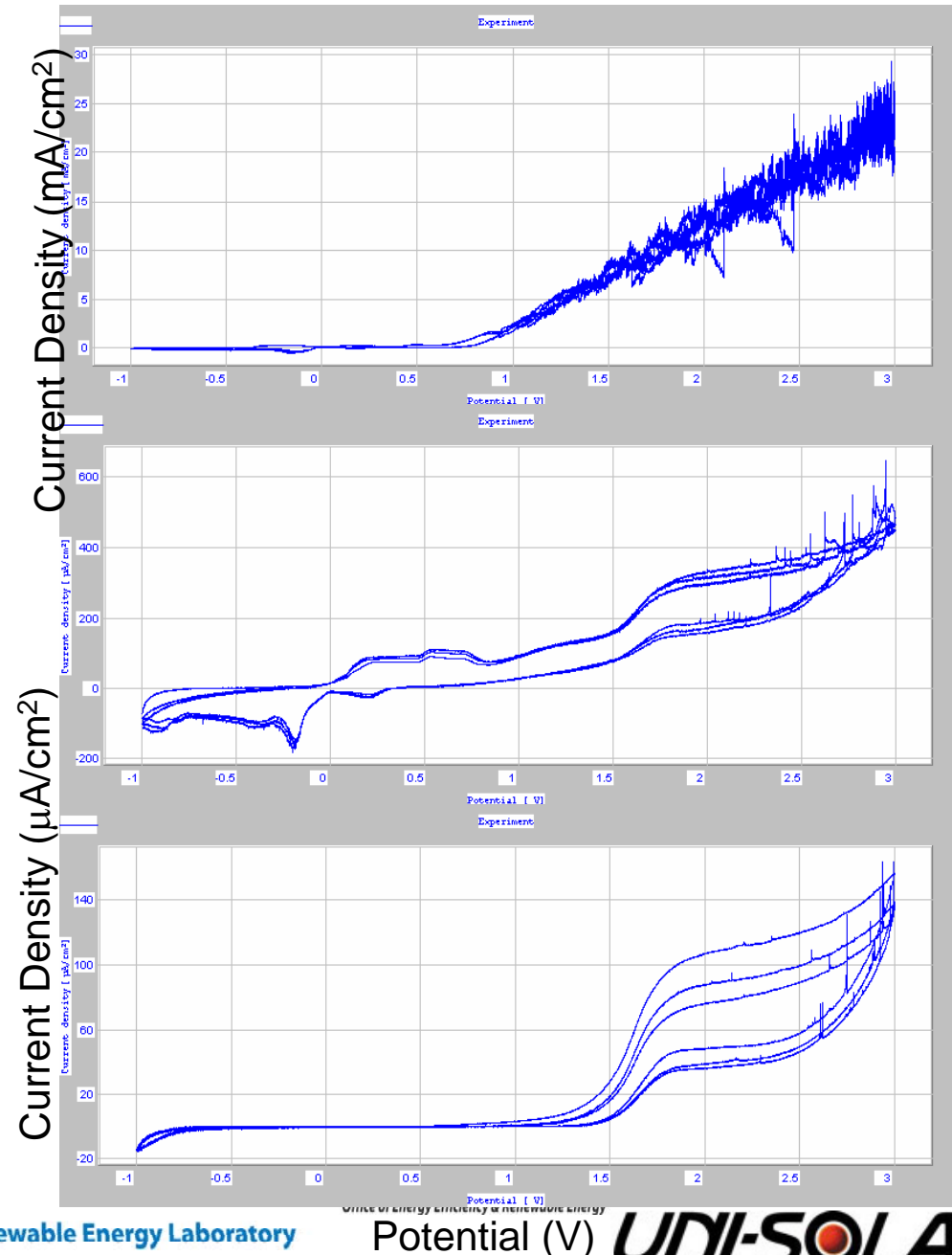


Potential (V)

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

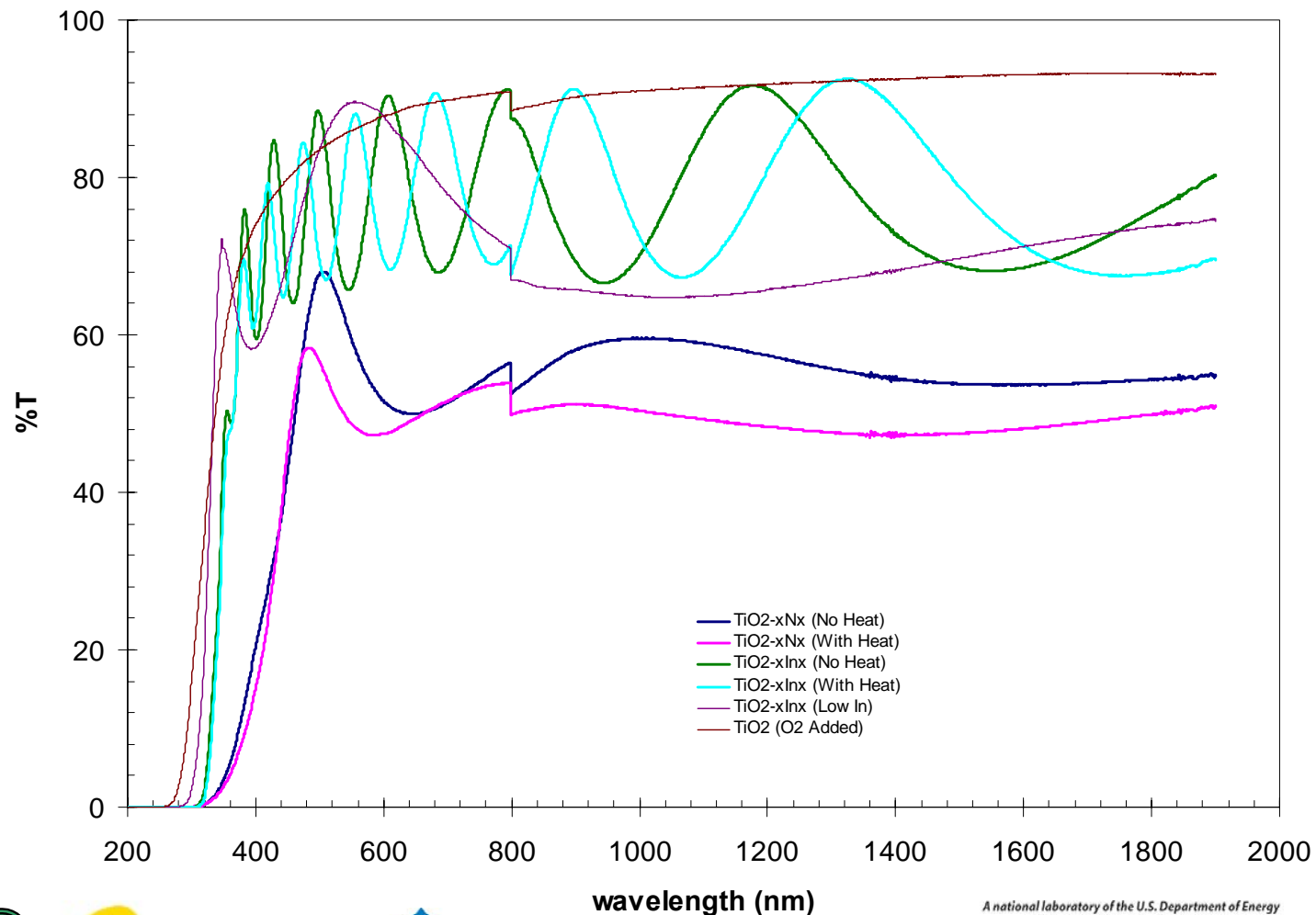
# TiO<sub>2-x</sub>In<sub>x</sub>

- (Top) Low amounts In dopant showed stability with larger current density
- Whereas (middle) shows lower current density with higher In conc., but still stable
- Photocurrent was observed only with the high levels of In
- For higher In sample, 4hr annealing improves stability of the film



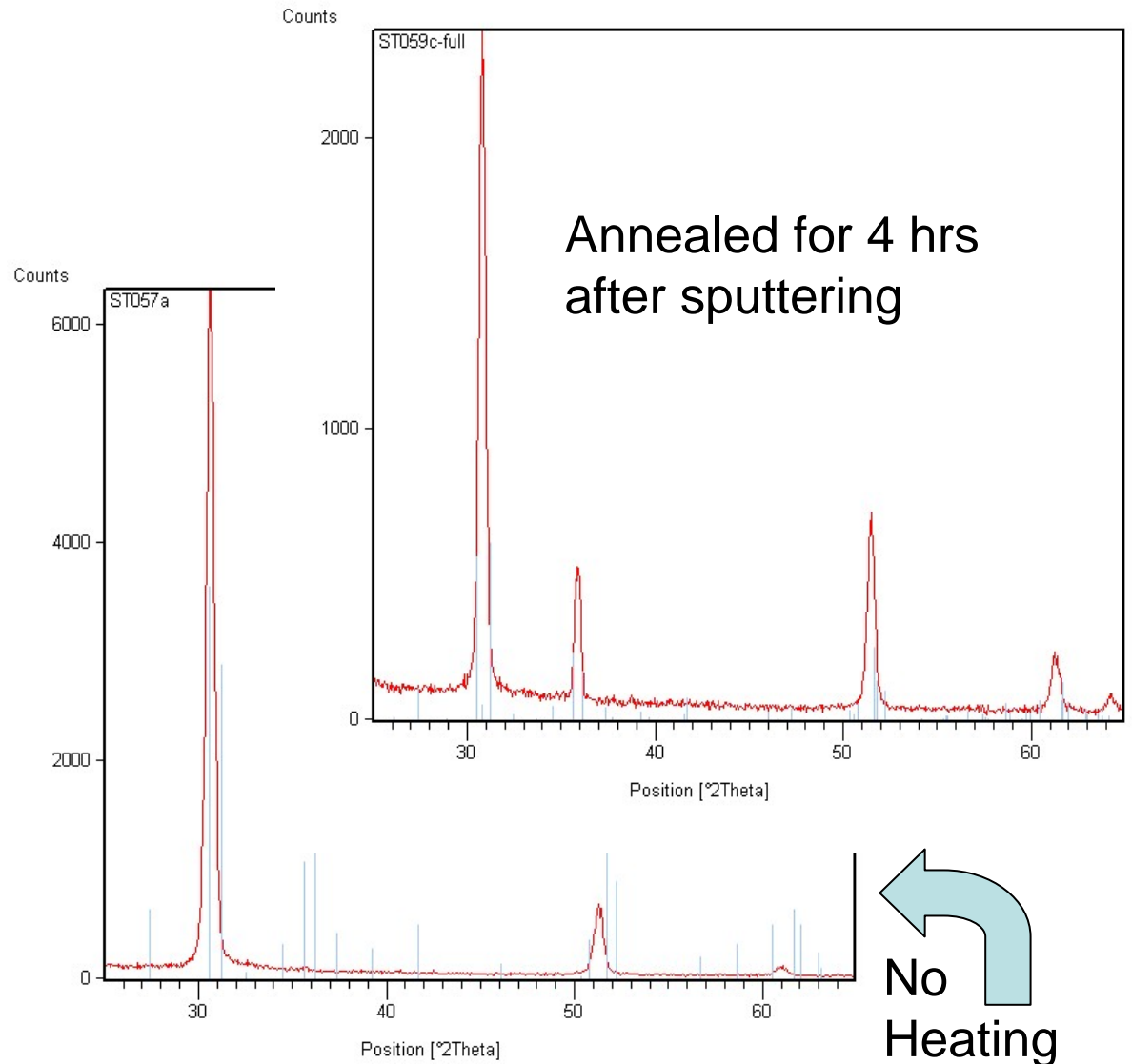
# Absorption Spectra for TiO<sub>2</sub>

- TiO<sub>2-x</sub>In<sub>x</sub> shows a similar absorption spectra to TiO<sub>2</sub>
- TiO<sub>2-x</sub>N<sub>x</sub> shows improved absorption in the visible spectrum



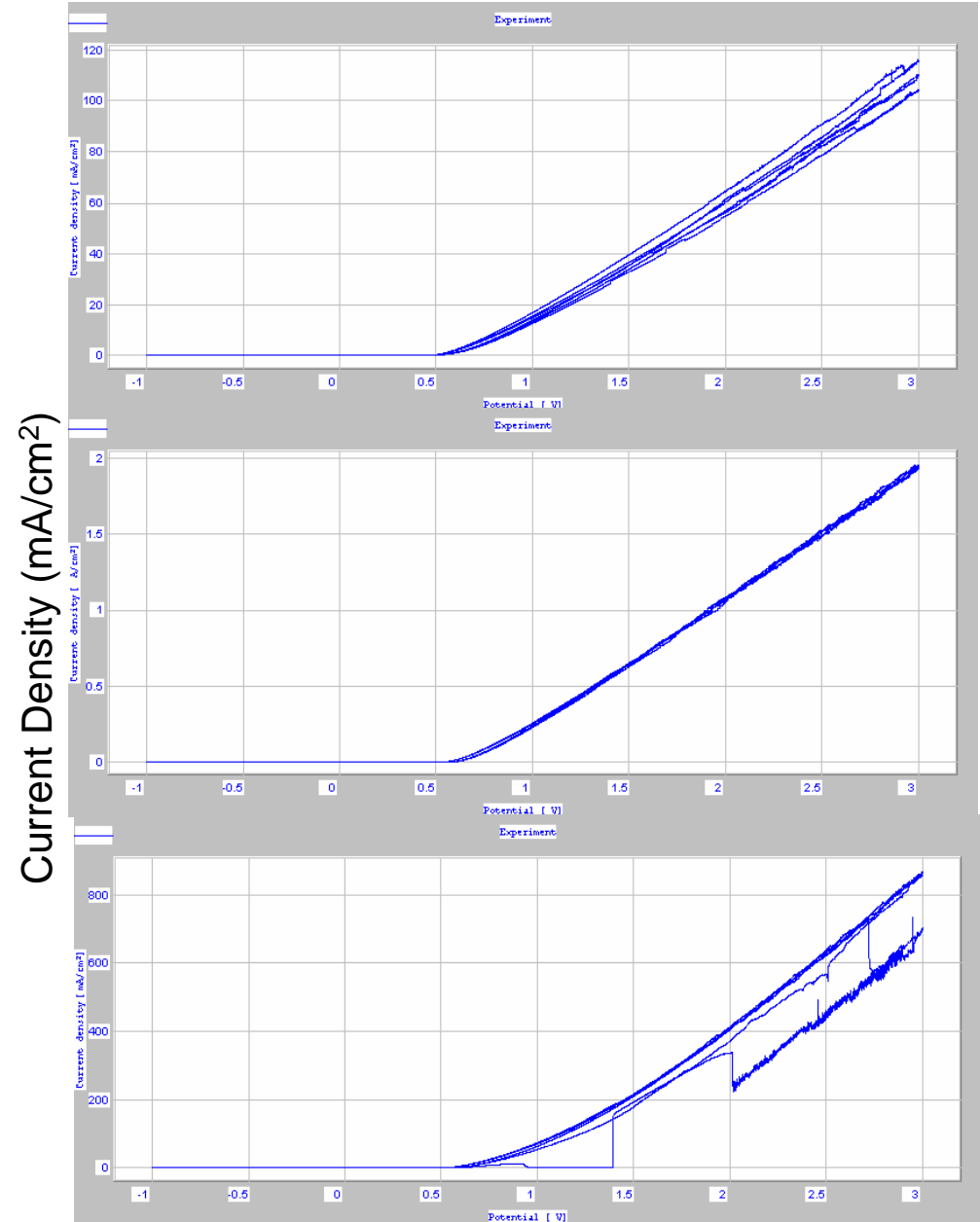
# X-ray Diffraction – TiO<sub>2</sub>

- TiO<sub>2-x</sub>In<sub>x</sub> exhibited crystallinity, which improved upon heating
- TiO<sub>2</sub> and TiO<sub>2-x</sub>N<sub>x</sub> showed no crystallinity with and without annealing
- Further testing will be performed to identify their structures



# I-V Measurements – Fe<sub>2</sub>O<sub>3</sub>

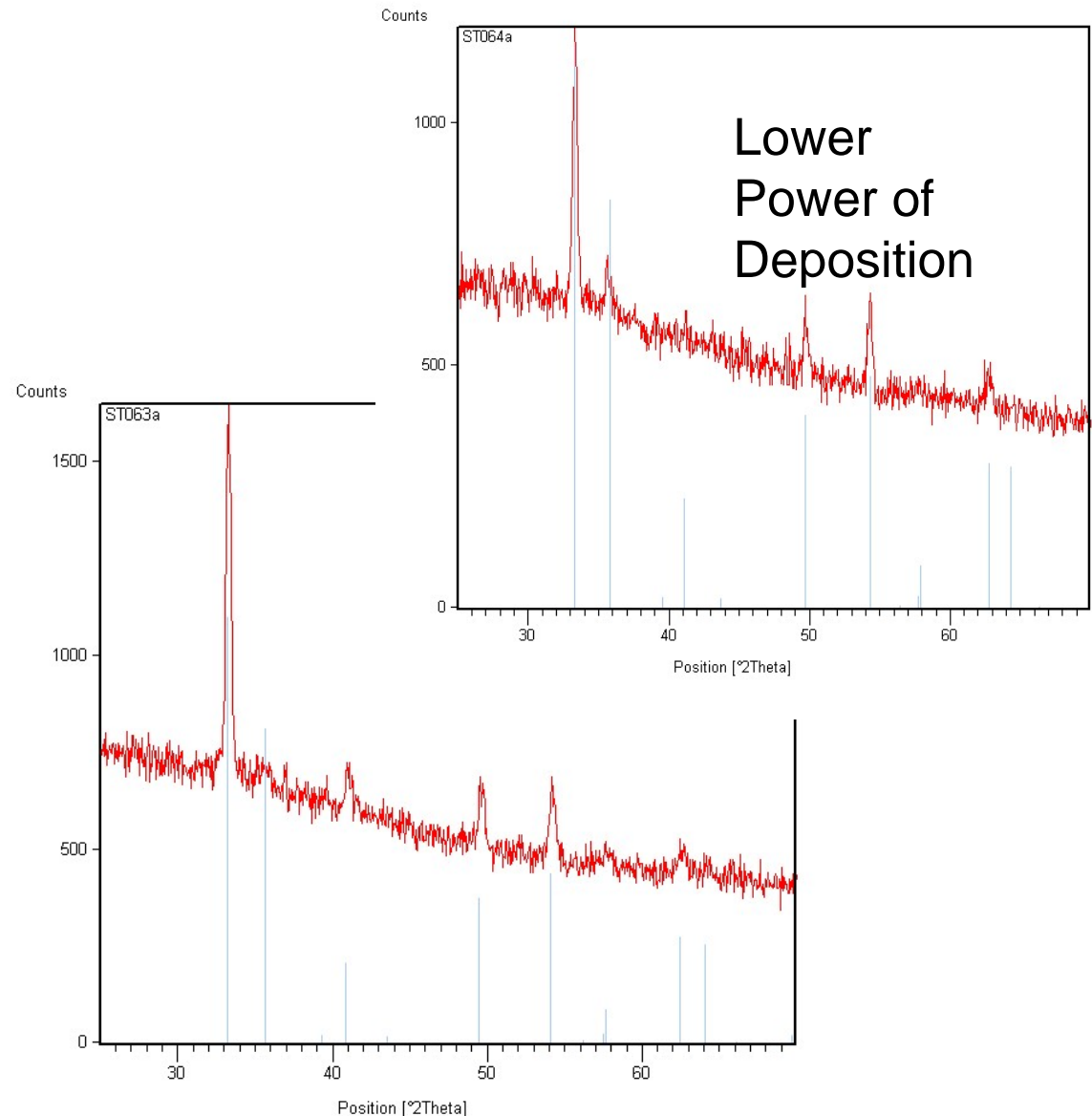
- Stable in 33% KOH standard solution
- Initial trials show high current density with excellent stability.
- I-V Curves for Fe<sub>2</sub>O<sub>3</sub> made with increasing power (50, 60, & 70 W)
- Lowest power showed minimal instability
- Absorption decreases with increased power used in deposition



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# X-ray Diffraction – Fe<sub>2</sub>O<sub>3</sub>

- Fe<sub>2</sub>O<sub>3</sub> exhibited crystallinity, which improved upon increased power during deposition
- Scans indicate the presence of hematite only in the films



# Responses to Previous Year Reviewers' Comments

- N/A
- New Project

# Future Work

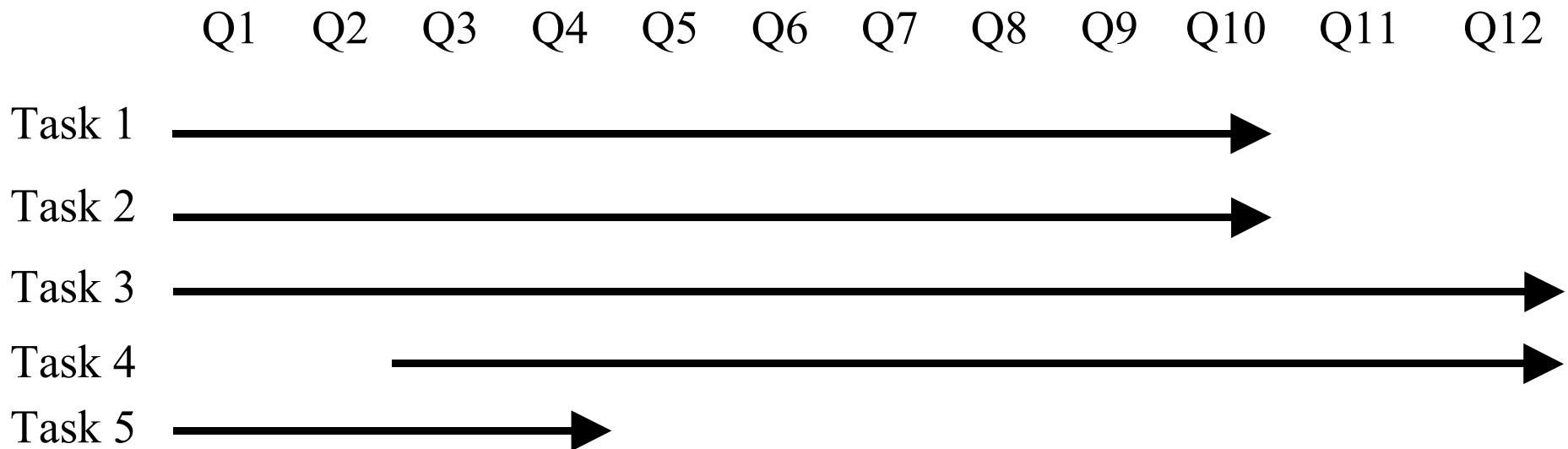
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Task 4: Fabrication of low-cost, durable and efficient immersion-type PEC cells and systems

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



# Publications and Presentations

“Development activities toward commercialization of photovoltaic hydrogen systems”, Liwei Xu, Presented at Northwest Ohio Alternative Energy Partnership Workshop, University of Toledo Student Union, Oct. 29, 2004.

“Renewable production of hydrogen from water using photoelectrochemical process”, Xunming Deng, presented at Purdue University “Hydrogen Economy” Colloquium, March 2, 2005.

Present MWOE’s superstrate-type PEC product at the Hydrogen and Fuel Cell Group Exhibit at Hannover Fair, Hannover, Germany, April 11-15, 2005

Demonstrated MWOE’s superstrate-type PEC product at COSI-Toledo (Toledo’s Science Museum) in its STRANGE MATTER special exhibit, Toledo, Ohio, April 17, 2005.

# 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 persons handling hydrogen

Other significant hazard related to this research is the handling of hazard gases such as  $\text{PH}_3$ ,  $\text{GeH}_4$ ,  $\text{SiH}_4$ ,  $\text{BF}_3$ ,  $\text{H}_2$  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.

# Collaborators

- **Midwest Optoelectronics, LLC**

Stanley Rubini

- **University of Toledo:**

Xunming Deng, Alvin Compaan, Robert Collins

Dean Giolando, Maria Coleman and A.H. Jayatissa

- **National Renewable Energy Laboratory**

John Turner

- **United Solar Ovonic Corp.**

Jeffrey Yang