Photoelectrochemical Water Systems for H_2 Production

2006 DOE Hydrogen, Fuel Cells & Infrastructure Technologies Program Review

John A. Turner, Todd Deutsch, Jeff Head, and Jennifer Leisch

National Renewable Energy Laboratory

jturner@nrel.gov 303-275-4270

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PDP 14

This presentation does not contain any proprietary or confidential information.

Overview

Timeline

- Project start date: 1991
- Project end date: tbd
- Percent complete: tbd

Budget

- Total project funding to-date
  - DOE share: $5.7M (~0.75 FTE + postdoc average)
- Funding received in FY05: $650k
- Funding for FY06: $140k.

Barriers

- Barriers addressed
  - ✓ **M. Materials Durability**
  - ✓ **O. Materials Efficiency.**
  - ✓ **N. Device Configuration Designs.**

Partners

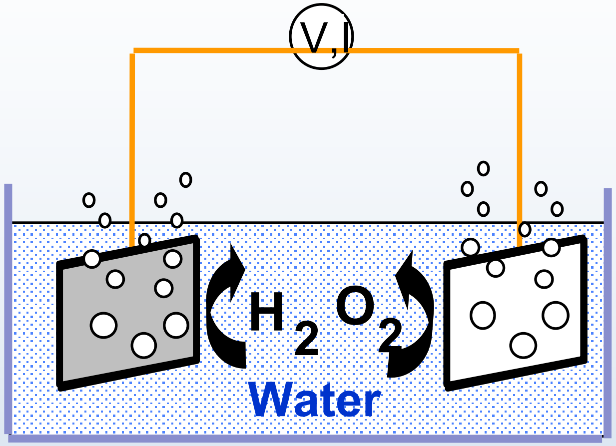
- Interactions/ collaborations
  - Colorado School of Mines
  - University of Colorado
  - Program Production Solicitation
    - MVSystems, Inc
    - Midwest Optoelectronics

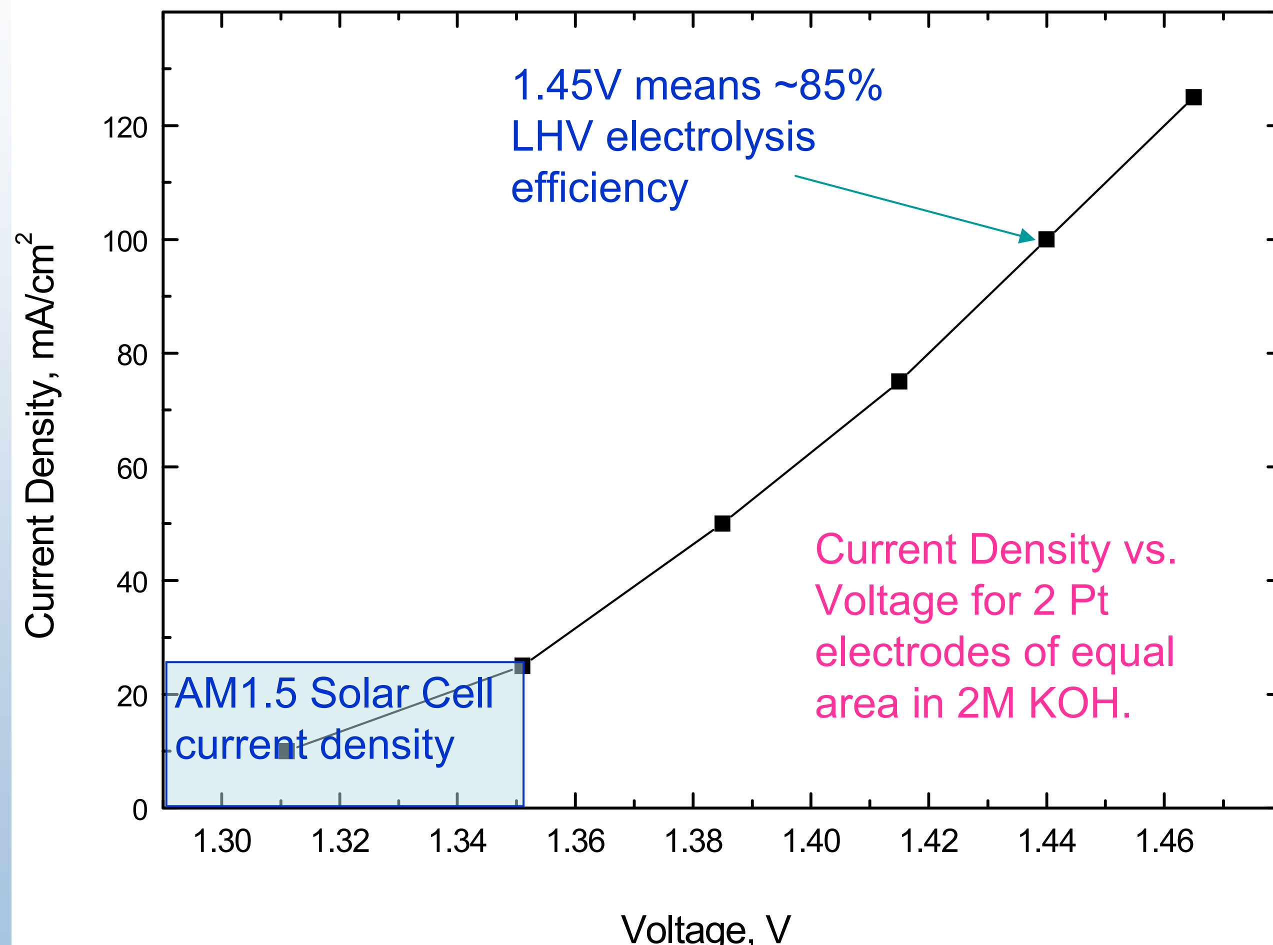
Photoelectrochemical Conversion
Goals and Objectives

The goal of this research is to develop a stable, cost effective, photoelectrochemical based system that will split water using sunlight as the only energy input. Our objectives are:

1. Identify and characterize new semiconductor materials that have appropriate bandgaps and are stable in aqueous solutions.
2. Study multijunction semiconductor systems for higher efficiency water splitting.
3. Develop techniques for the energetic control of the semiconductor electrolyte interface, and for the preparation of transparent catalytic coatings and their application to semiconductor surfaces.
4. Identify environmental factors (e.g., pH, ionic strength, solution composition, etc.) that affect the energetics of the semiconductor, the properties of the catalysts, and the stability of the semiconductor.
5. Develop database to house a library of the material properties being discovered by the DOE program.

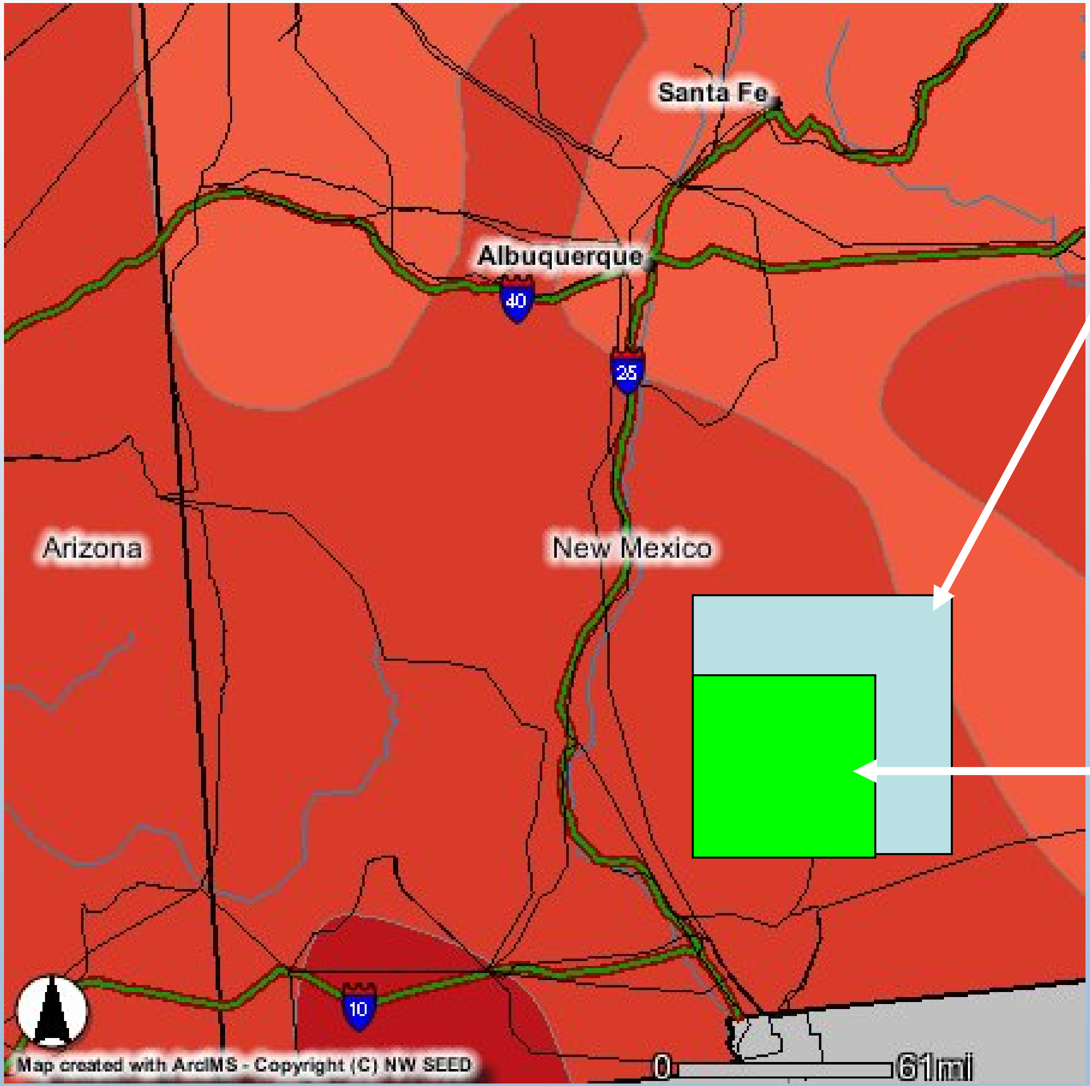
Higher efficiency from PEC devices (as compared to PV/electrolysis) stems from the lower operational current density when using direct solar light.





O. Khaselev, A. Bansal and J. A. Turner, *International Journal of Hydrogen Energy*, **26**, p 127-132 (2001).

Hydrogen From Solar Energy and Water: PV/Electrolysis vs. PEC Direct Conversion

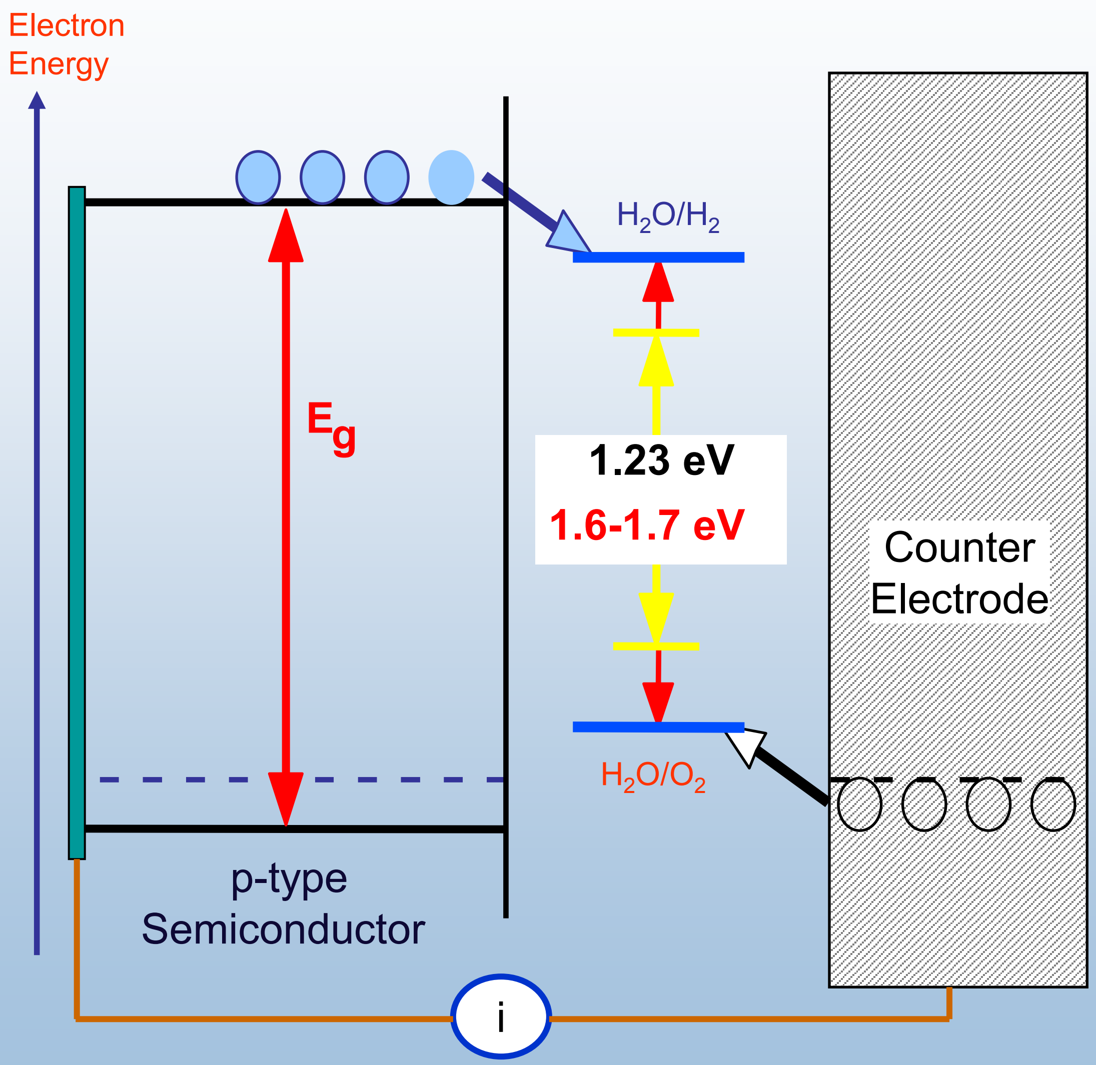


PV panel area to produce hydrogen for current US fleet (10% system, 70% electrolysis efficiency)

PEC direct conversion system for same amount of hydrogen

Material Challenges *(the big three)*

Characteristics for Ideal Photoelectrochemical Hydrogen Production Material



- **Efficiency –** the band gap (E_g) must be at least 1.6-1.7 eV, but not over 2.2 eV; must have high photon to electron conversion efficiency.
- **Material Durability –** semiconductor must be stable in aqueous solution.
- **Energetics –** the band edges must straddle H_2O redox potentials (Grand Challenge)

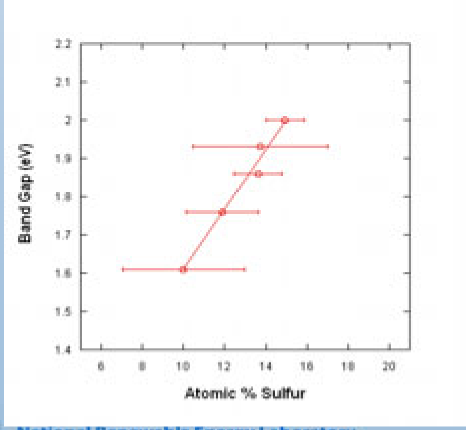
All must be satisfied <u>simultaneously</u>

Approach: High Efficiency Materials and Low-cost Manufacturing.

PEC devices must have the same internal photon-to-electron conversion efficiency as commercial PV devices.

- III-V materials have the highest solar conversion efficiency of any semiconductor material.
  - Large range of available bandgaps
  - ….but
    - Stability an issue – nitrides show promise for increased lifetime
    - Band-edge mismatch with known materials – tandems an answer

- I-III-VI materials offer high photon conversion efficiency and possible low-cost manufacturing.
  - Synthesis procedures for desired bandgap unknown.
  - ….but
    - Stability in aqueous solution?
    - Band-edge mismatch?



- Other thin-film materials with good characteristics
  - SiC: low-cost synthesis, stability
  - SiN: emerging material

Approach: Materials Summary

The primary task is to synthesize the semiconducting material or the semiconductor structure with the necessary properties. This involves material research issues (material discovery), multi-layer design and fabrication, and surface chemistry. Activities are divided into the task areas below – focus areas in *black*:

- *GaPN - NREL (high efficiency, stability)*
- *$CuInGa(Se,S)_2$ - UNAM (Mexico), NREL (Low cost)*
- *Silicon Nitride – NREL (protective coating and new material)*
- $GaInP_2$ - NREL (fundamental materials understanding)
- Energetics
  - Band edge control
  - Catalysis
  - Surface studies

III-V Nitrides for PEC Water Splitting Systems: $GaP_{1-x}N_x$

- GaN
  - Capable of water-splitting and stable
  - Band gap direct but too wide (~3.4 eV)
- GaP
  - Band edges almost aligned
  - Band gap indirect and too wide (~2.3 eV), but better.
- $GaP_{1-x}N_x$
  - Addition of small amounts of N causes GaP band gap to narrow (bowing) and transition to become direct
  - Nitrogen enhances stability

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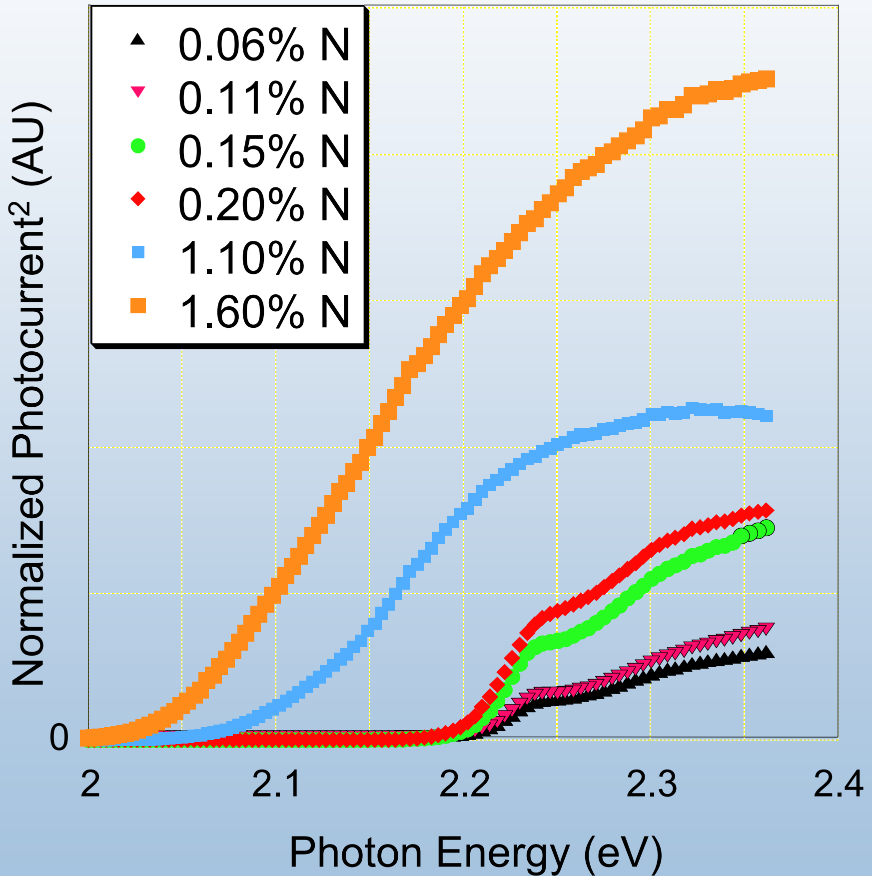
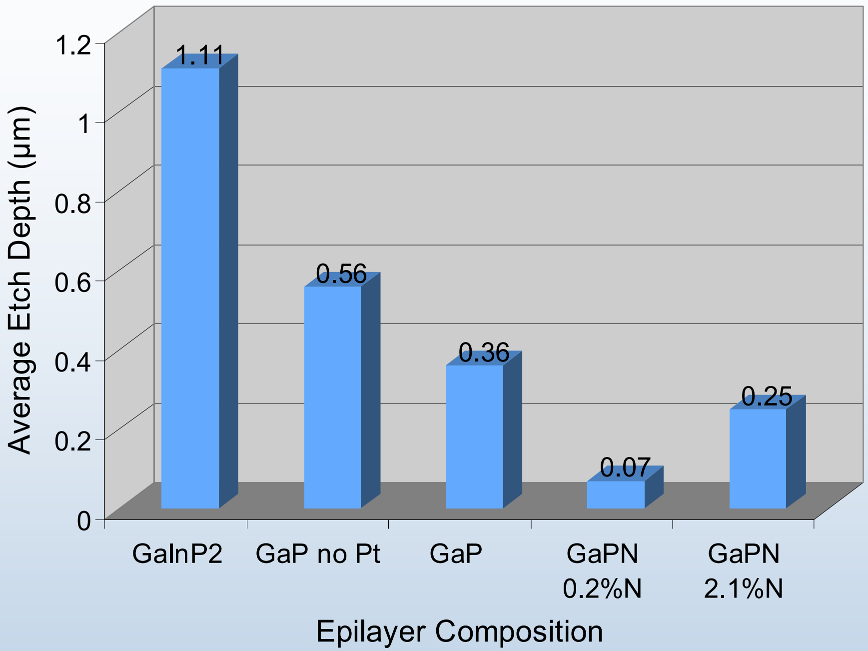
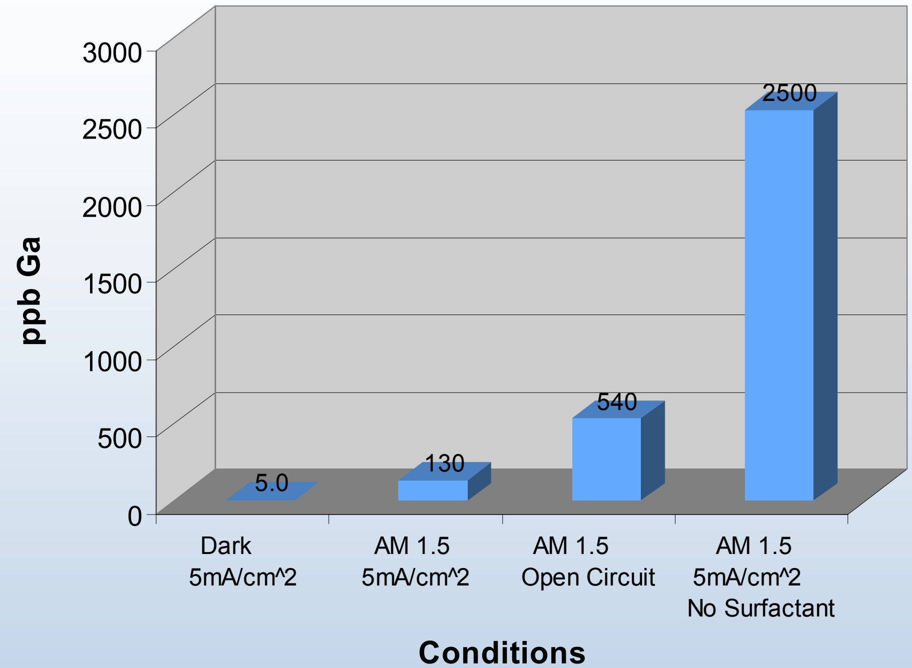
$GaP_{1-x}N_x$ Epilayer Direct Band Gap

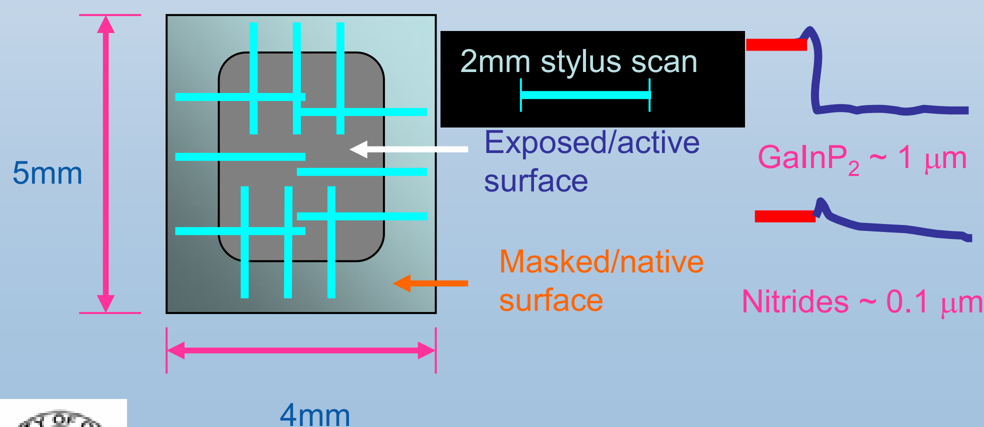


Goal: Stable III-V nitride material

GaPN Stability measured by profilometry and by ICP-MS of solution



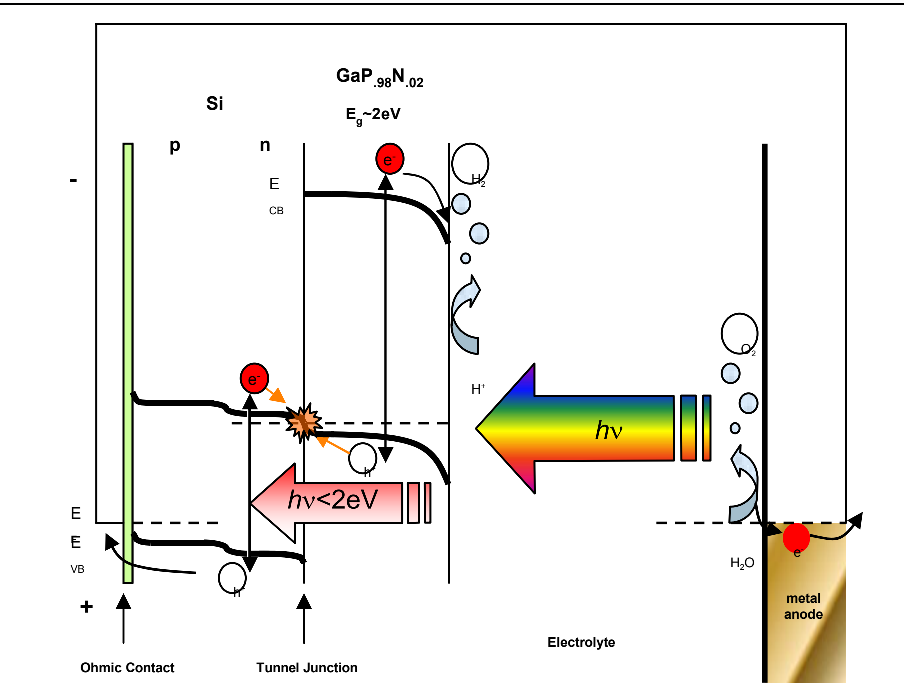




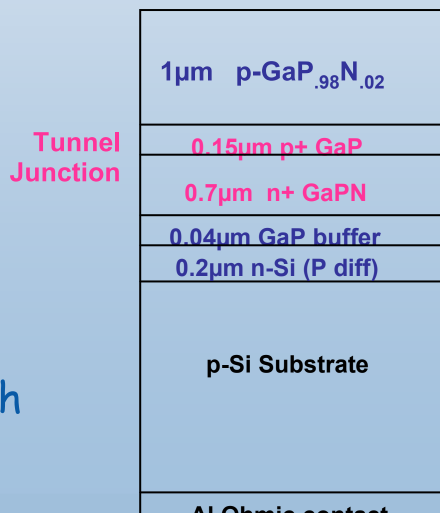
- Photocathode durability testing
  - 5mA/cm^2, AM 1.5, 24 hours, 3M H_2SO_4, pulsed Pt treatment.
  - Ga content of solutions by ICP-MS
  - Etching by profilometry
- Represents ~300 hrs of stability for 1 um layer

Goal: III-V nitride tandem water splitting cell

GaPN:Si Tandem cell



- ~ 1% water splitting efficiency.
- Results complicated by compositional variation across the sample



Direct Eg (eV)
Nitrogen%

20mm × 25mm

1.99 2.2%	2.00 2.1%	2.00 2.1%	2.01 2.0%	2.01 2.0%
2.00 2.1%	2.01 2.0%	2.01 2.0%	2.02 1.9%	2.02 1.9%
2.01 2.0%	2.02 1.9%	2.02 1.9%	2.02 1.9%	2.03 1.8%
2.03 1.8%	2.03 1.8%	2.03 1.8%	2.03 1.8%	2.04 1.7%

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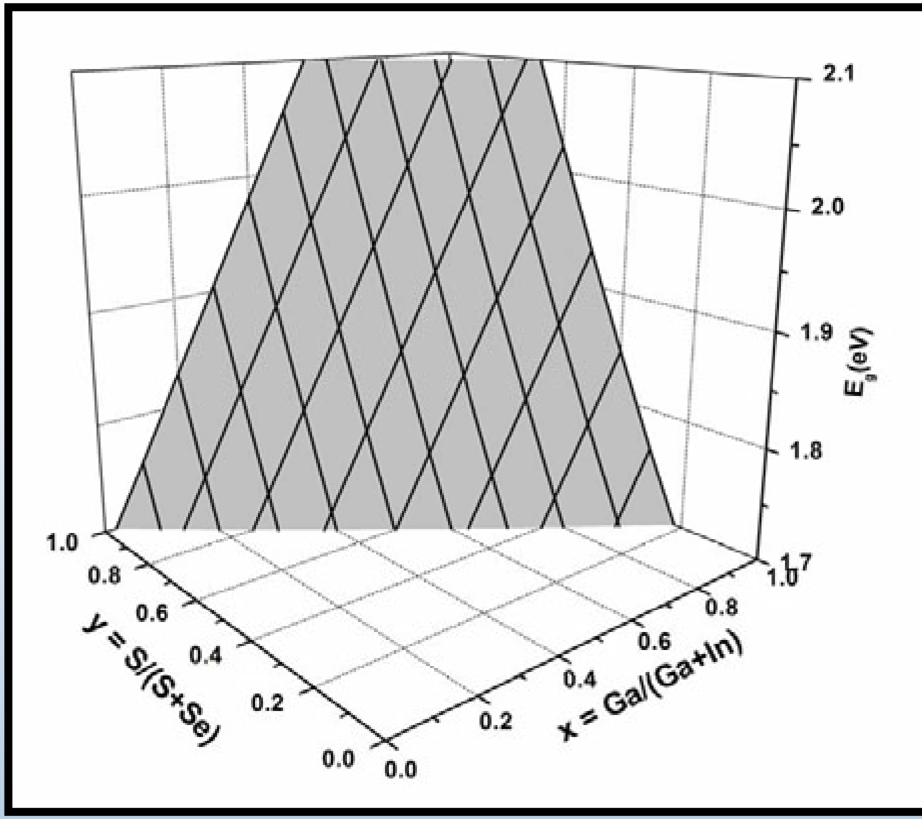
Goal: Evaluation of high efficiency thin-film CIS-based material

Electrodeposited CIGSS

- CIS Material System: $CuInSe_2$ – $CuGaS_2$
  - E_g range: 1.0 – 2.5eV
- $CuGaSe_2$: E_g = ~1.7
- High PV efficiencies in this system
- Potential low-cost low energy deposition
- Two Configurations:
  - Single materials
  - As a layer in a multijunction system



Relationship of bandgap to alloy composition. Gray area represents compositions that produce bandgaps in the range 1.7 – 2.1eV.

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Goal: Evaluation of high efficiency thin-film material and thin-film based tandem cell.

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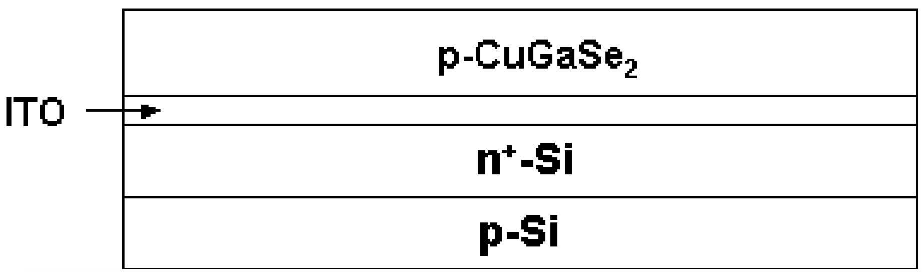
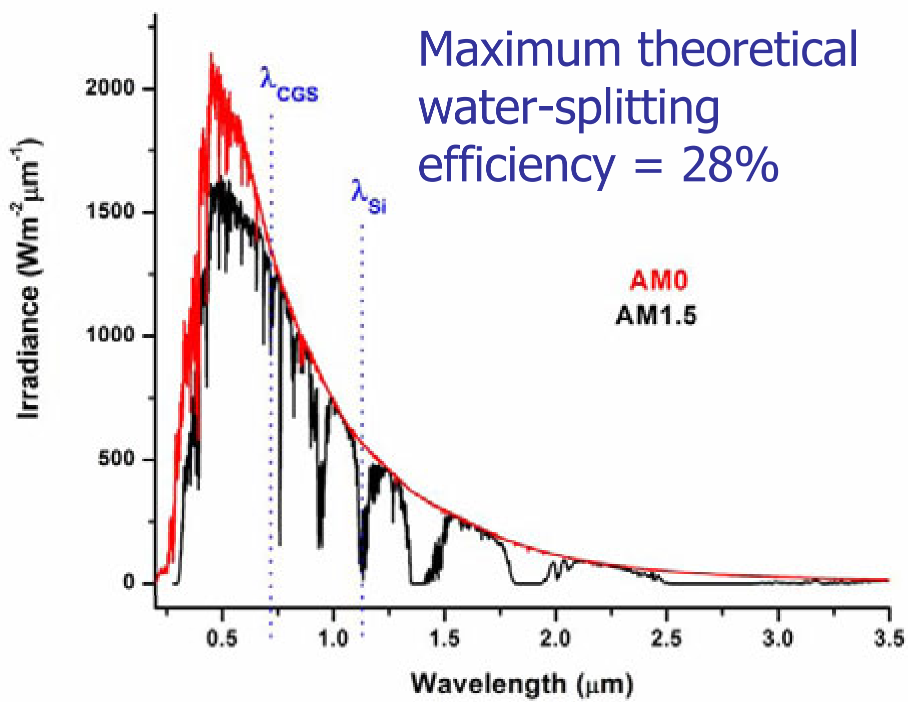
Tandem Cell configuration

CGS grown by thermal evaporation





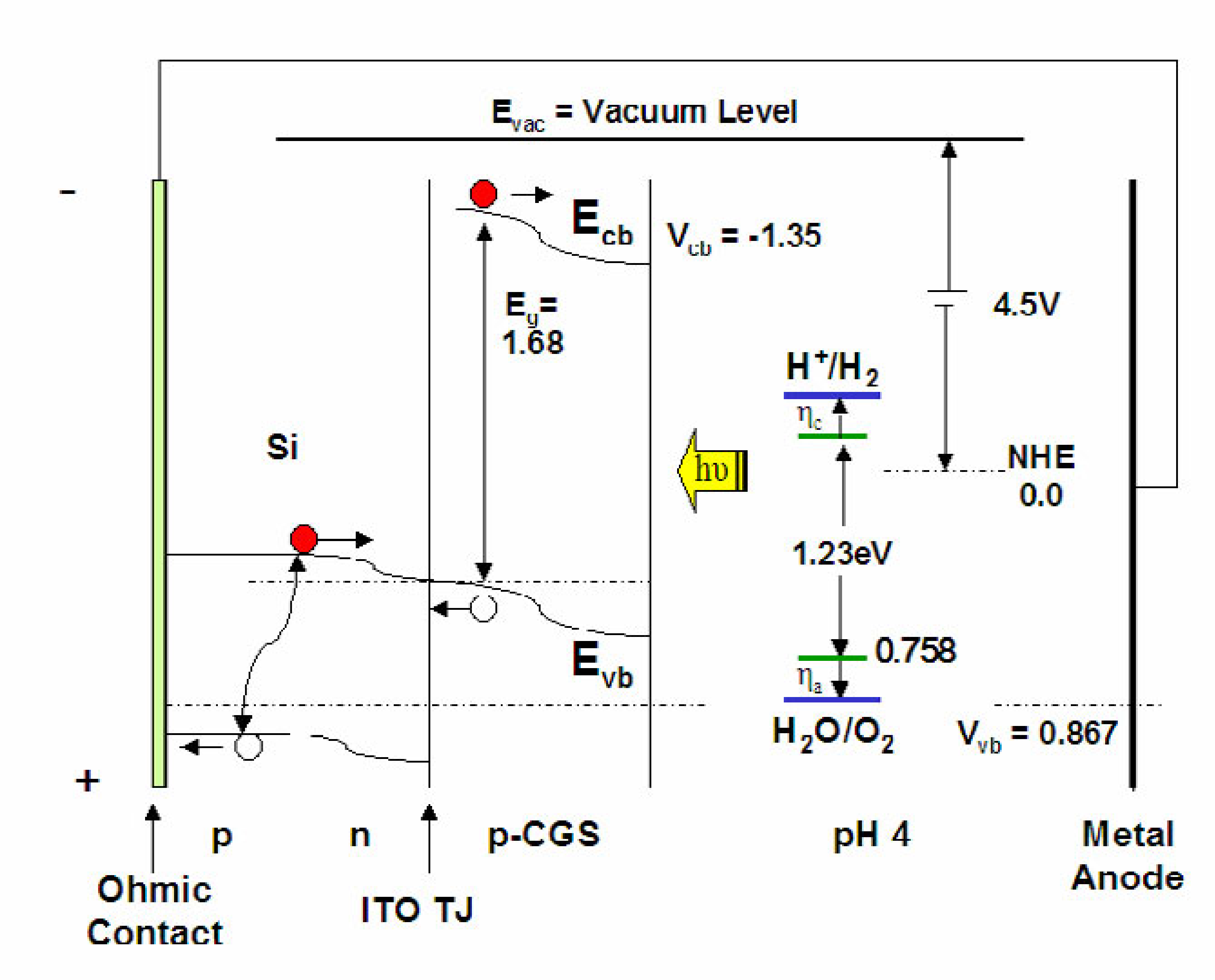
Maximum theoretical water-splitting efficiency = 28%

CGS: 1.3µm
ITO: 150nm

Results – Band Energy Diagram

Energetics say:
H_2O Splitting, but ver
low currents

Why?
- Poor ITO TJ
- Kinetics for H_2
- Recombination
- Band Shifting
- Corrosion



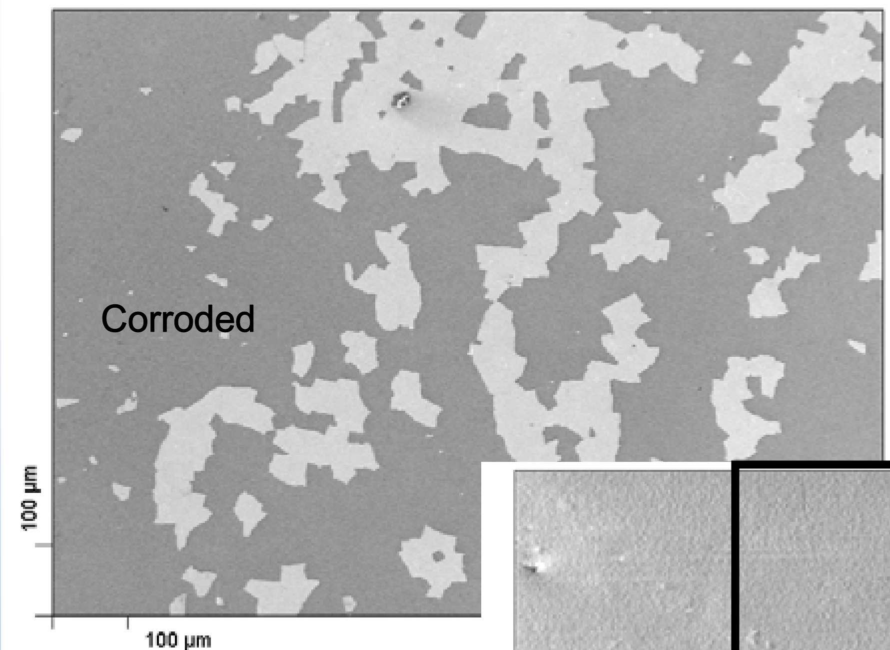
Results – Stability

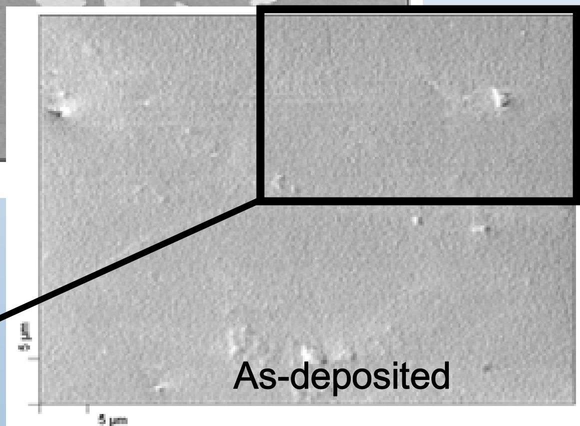
Visible cracks lead to undercutting of the CGS layer.

The high temperature CGS vapor deposition process damages the ITO layer. Acid solution dissolves the ITO.

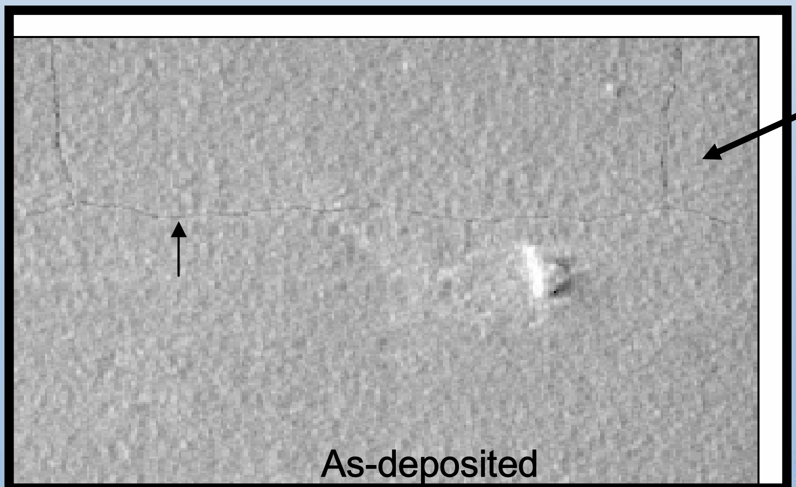
CGS on Mo substrates shows good stability.

Electrodeposition may be a better approach.





$2 mA/cm^2$, $3M\ H_2SO_4$, 2hrs.
$100 mW/cm^2$ W Illumination
$.03 mL/min\text{-}cm^2\ H_2$ Evolution



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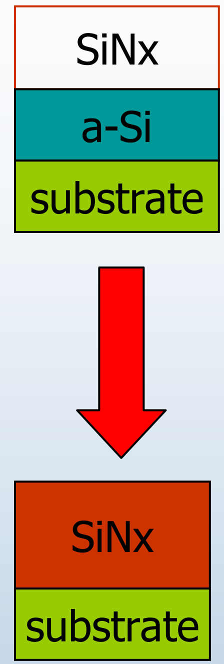
<u>Goal: Evaluation of SiN films for PEC devices.</u>

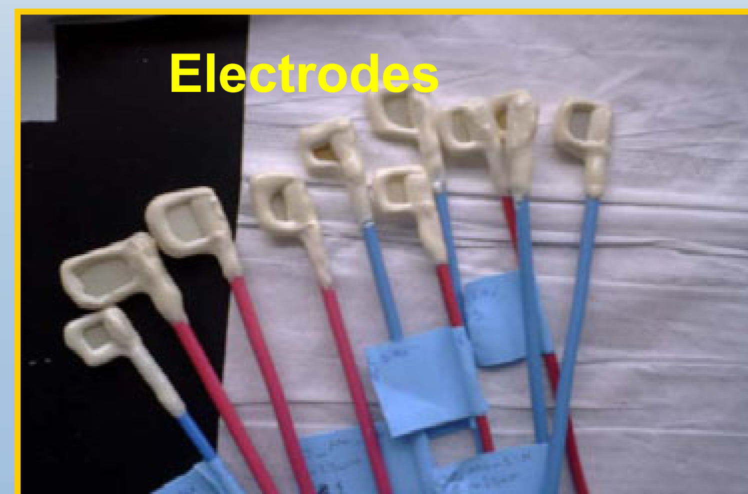
Thin-Film Silicon Nitride for PEC devices

- Known stable material
- Synthesis conditions can produce transparent and nontransparent films, possibilities of:
  - Corrosion resistant transparent coating
  - Direct water splitting system as a single device or as part of a tandem.
- Low-cost, high volume synthesis possibilities



Corrosion Protection

Water-splitting



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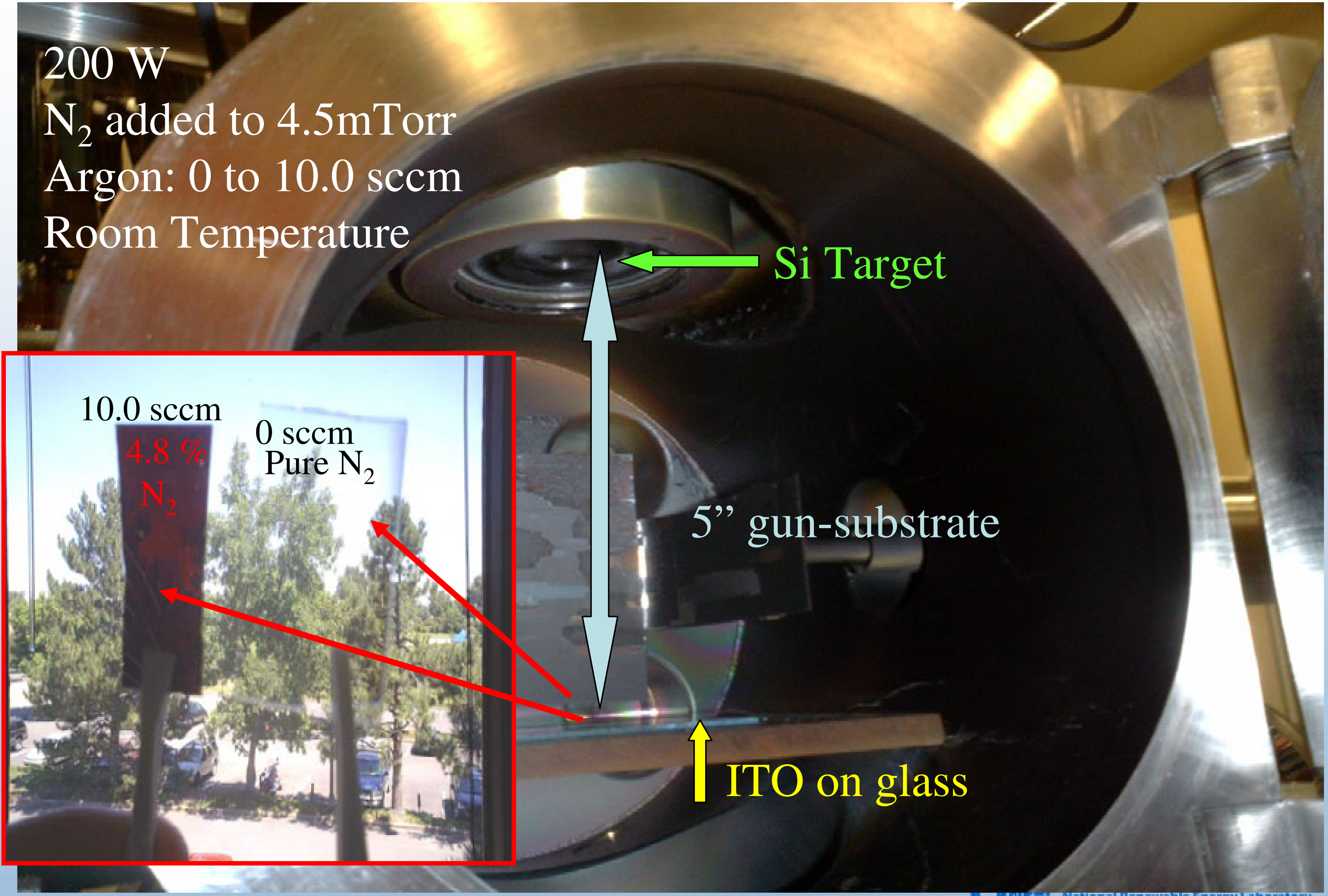
Thin Film Silicon Nitride from DC Magnetron Sputtering

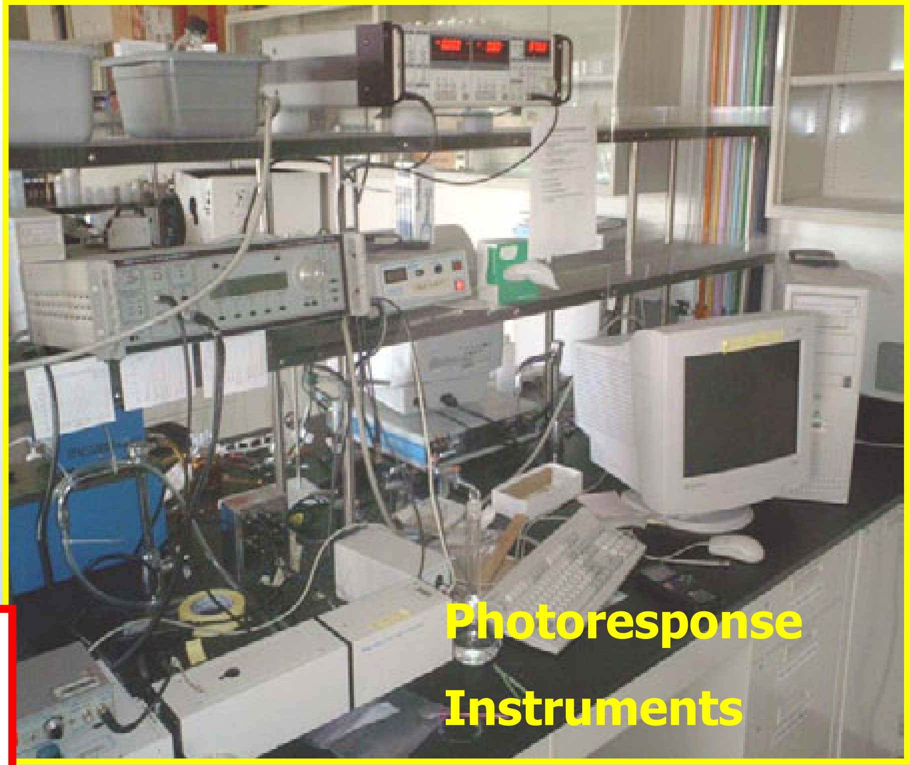
Sputter silicon target in nitrogen atmosphere

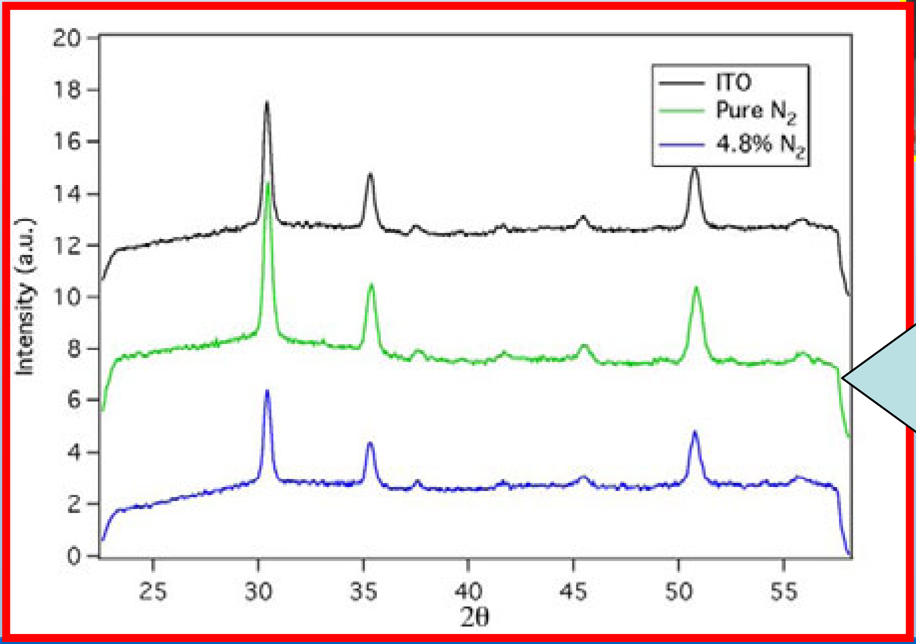


Goal: Evaluation of SiN films for PEC devices.

Analysis Techniques

- Electrochemical
- Photo-response
- Reflection/ transmission spectroscopy
- X-ray
- Raman spectra analysis





X-ray diffraction measurements indicate that the films are amorphorus

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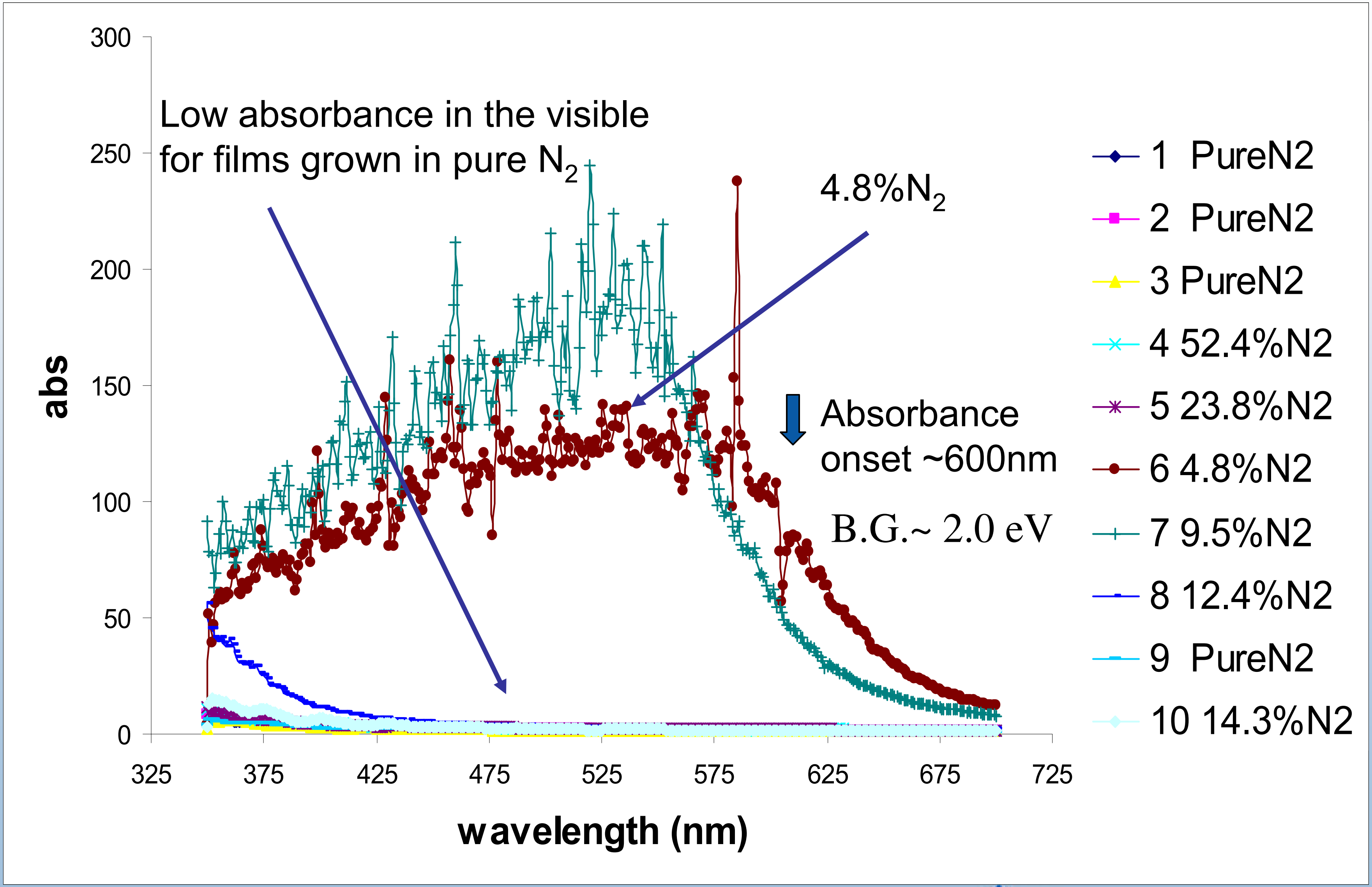
Goal: Evaluation of SiN films for PEC devices.

Initial absorbance measurements



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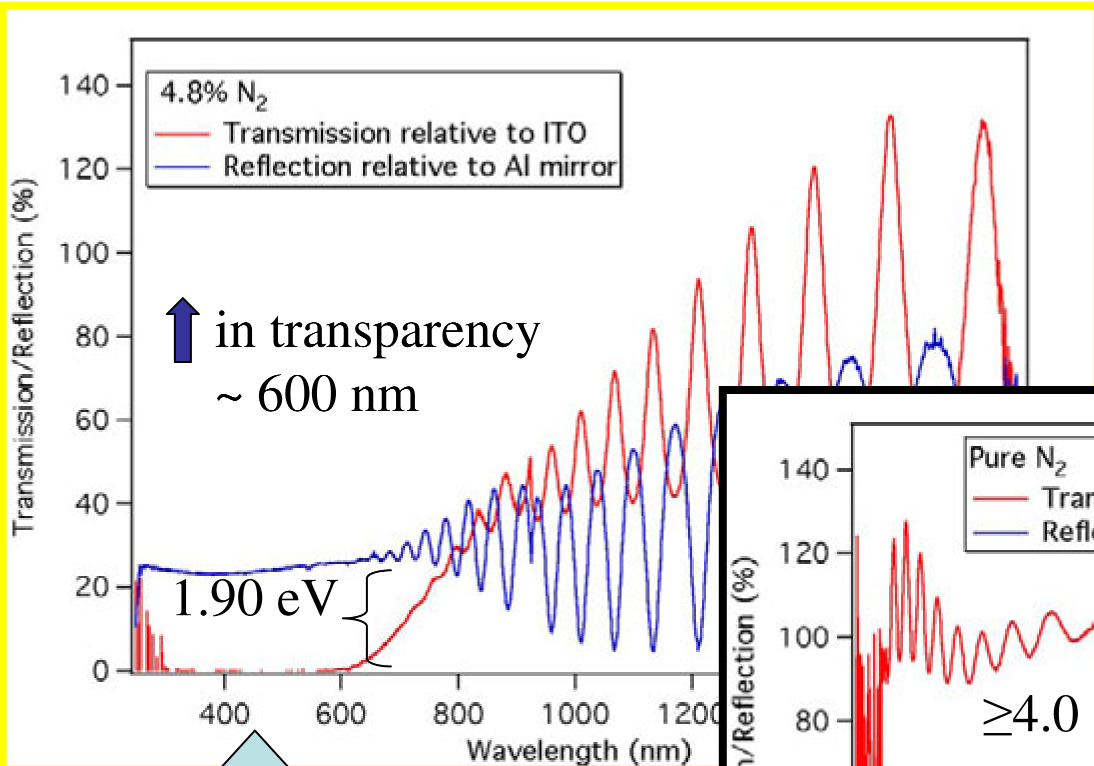
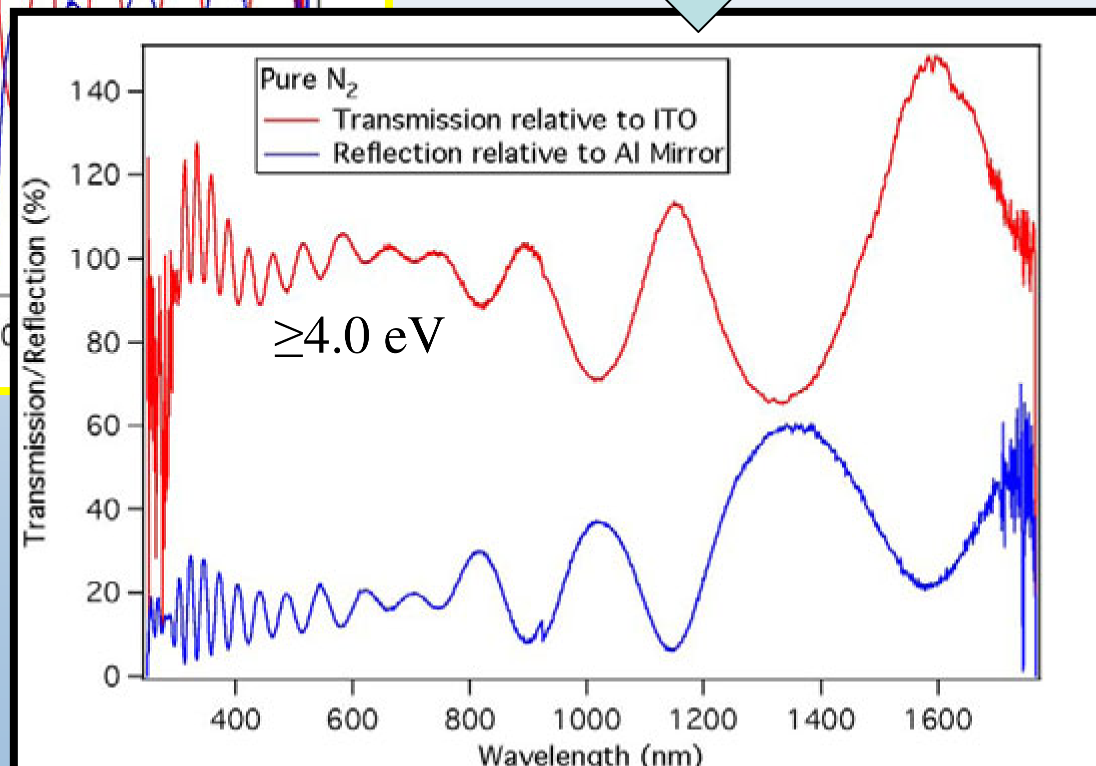
Goal: Evaluation of SiN films for PEC devices.

Optical Transmission/Reflection



High transparency for films grown in pure nitrogen



1.9eV absorption edge for film grown in 4.8% N, (Ar remainder).

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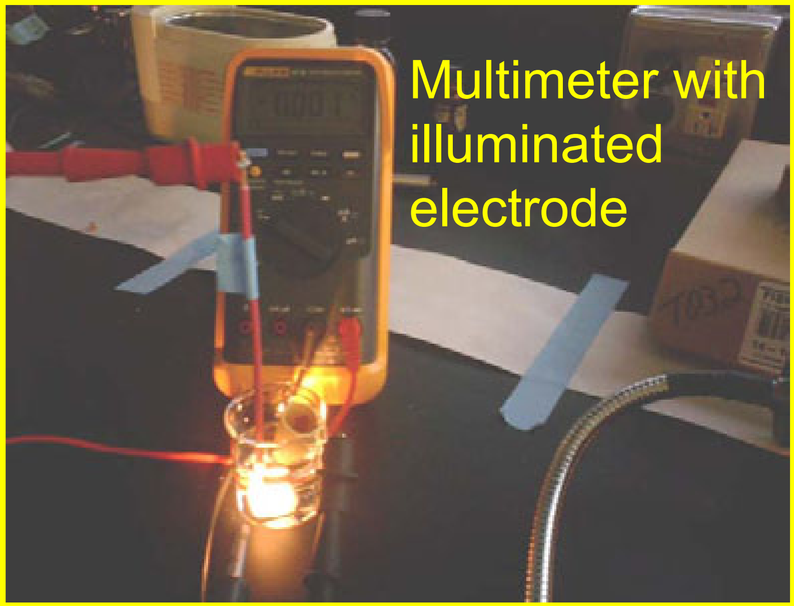
Goal: Evaluation of SiN films for PEC devices.

Photo-effects for as-grown SiN

- Films grown in pure nitrogen show very little photoeffect (transparent).
- Film grown in 4.8% N_2 shows largest ΔV = -131mV
- n-type response
- Four point conductivity ≥ 10^7 Ω/square



Sample	Pure N_2	Pure N_2	Pure N_2	52.4% N_2	23.8% N_2	14.3% N_2	9.52% N_2	**4.8% N_2**
Dark	-0.008	-0.059	-0.011	-0.093	-0.02	-0.018	-0.012	**-0.23**
Light	-0.031	-0.083	-0.021	-0.128	-0.036	-0.064	-0.035	**-0.361**
ΔV	-0.023 V	-0.024 V	-0.01 V	-0.035 V	-0.016 V	-0.046 V	-0.023 V	**-0.131V**

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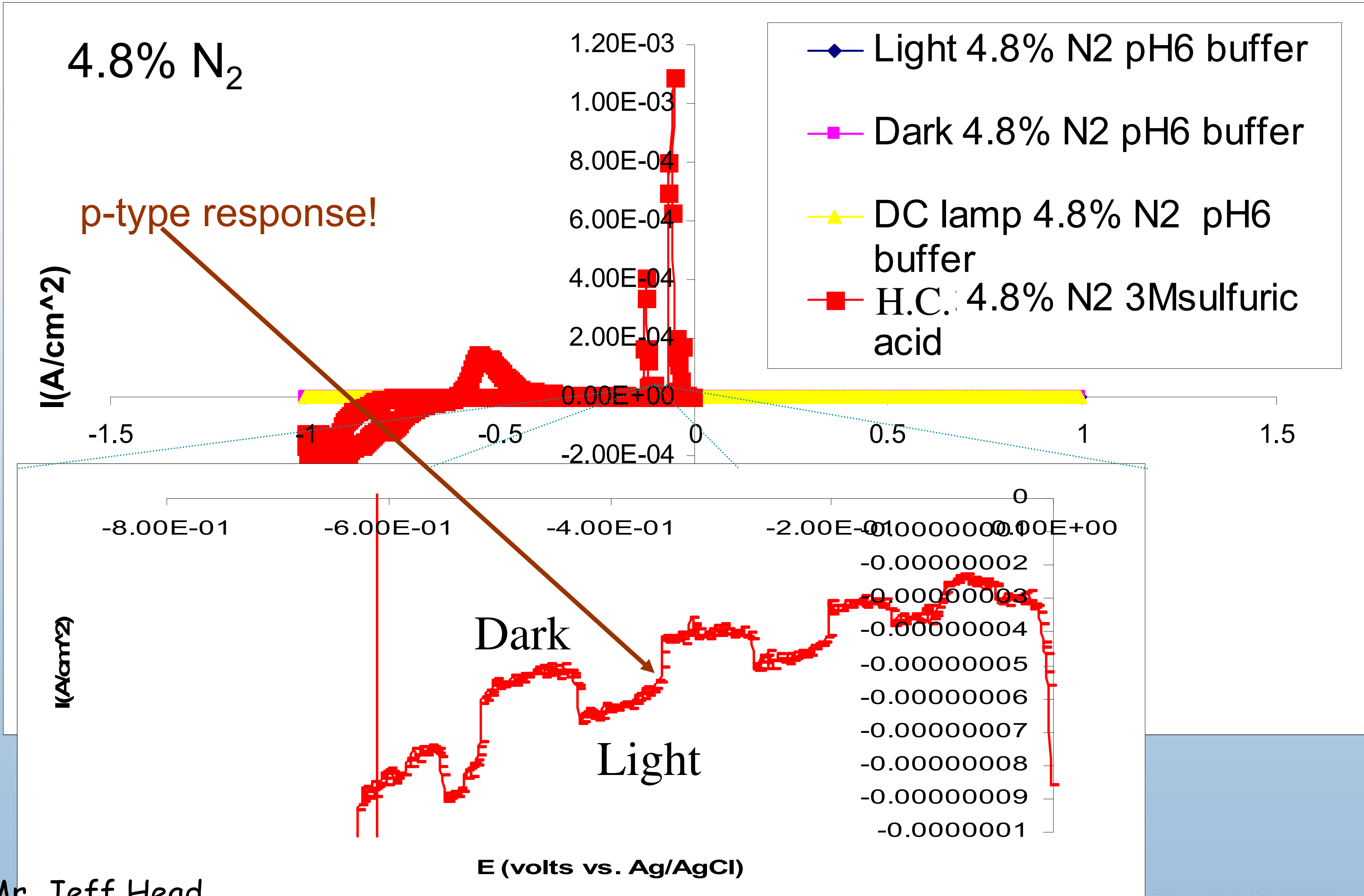
Goal: Evaluation of SiN films for PEC devices.

Photocurrent Measurements

Shows a p-type response in Acid



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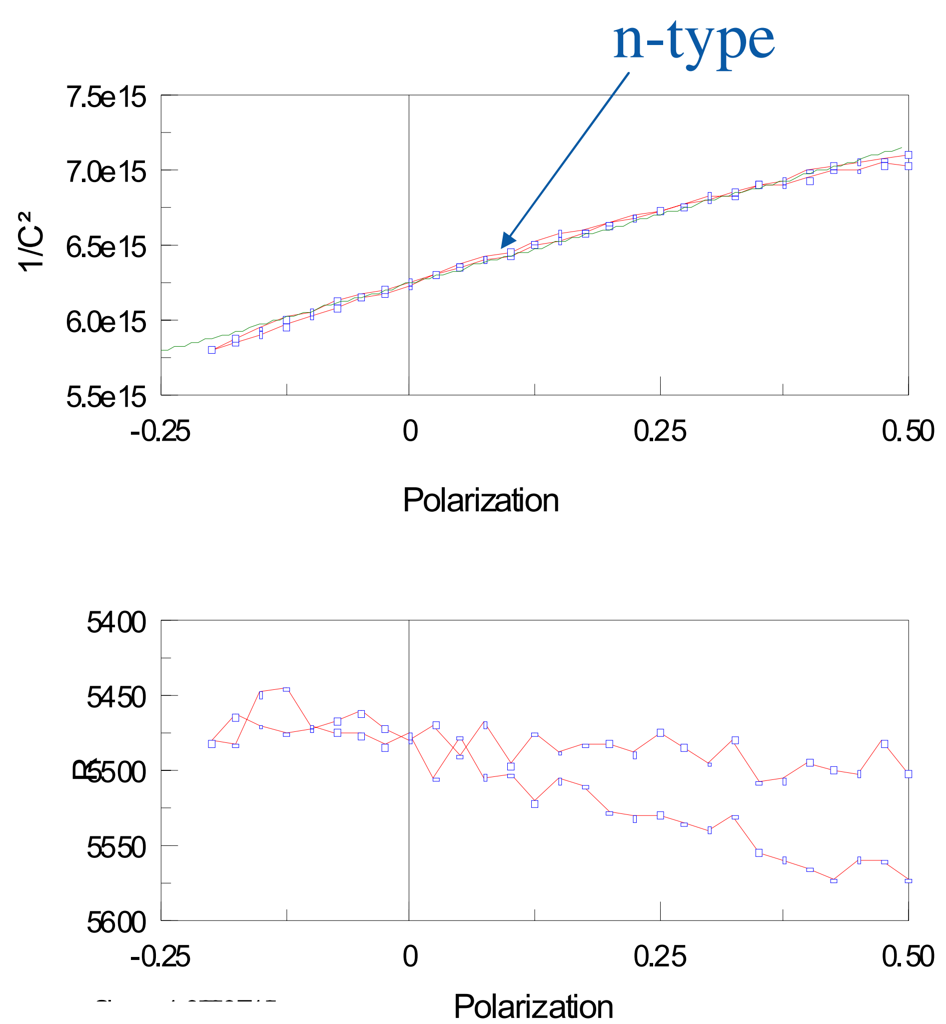
Goal: Evaluation of SiN films for PEC devices.

Mott-Schottky Analysis

- Slope indicates n-type semiconductor
  - 4.8% N_2 = -1.45 Vfb
  - significant variation between samples
- Doping density ranges between 10^{15} to $10^{17}/cm^3$.
- Material is probably highly compensated which gives rise to its dual n- and p-type response



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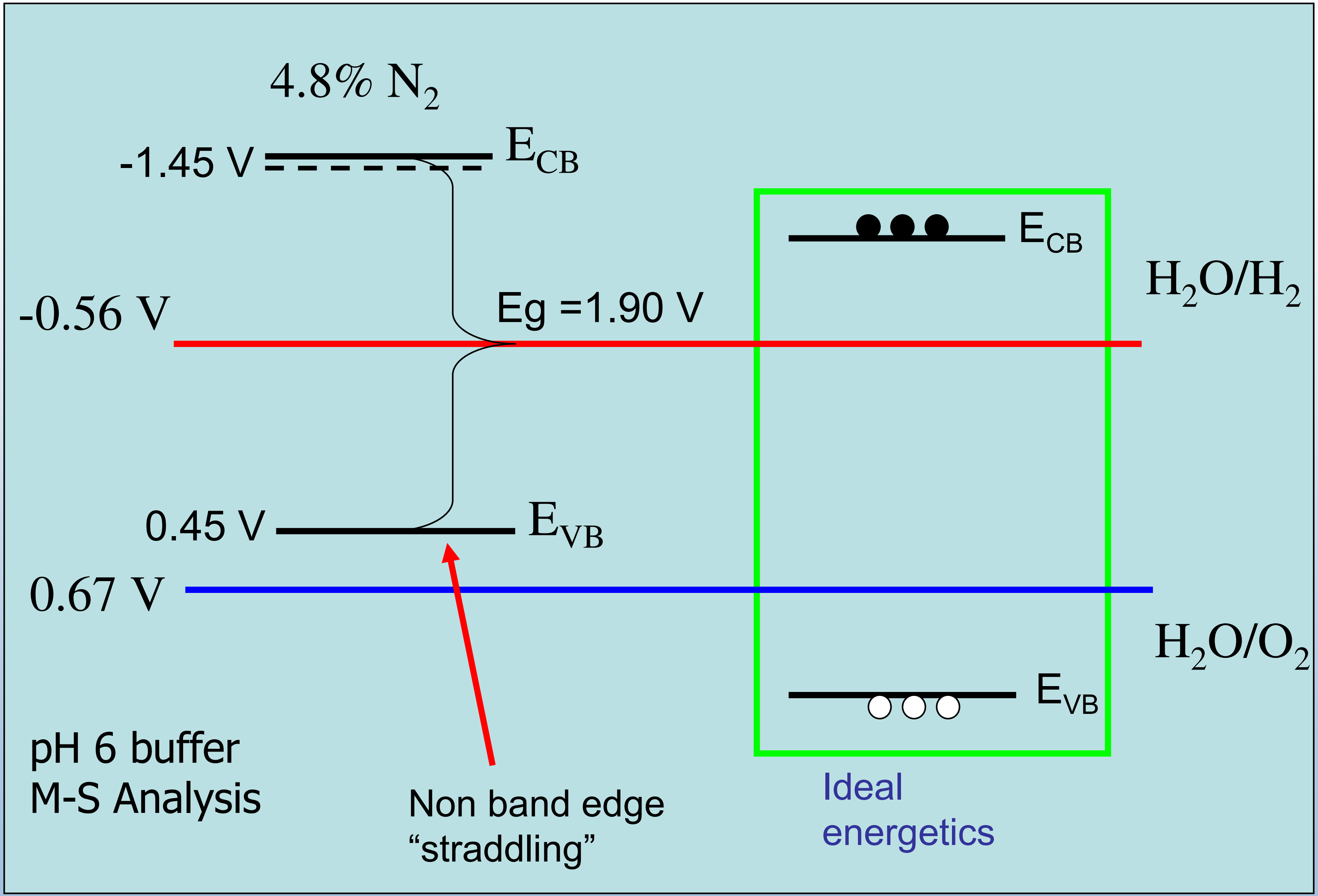
Goal: Evaluation of SiN films for PEC devices.

Band Edge Positions (Preliminary)



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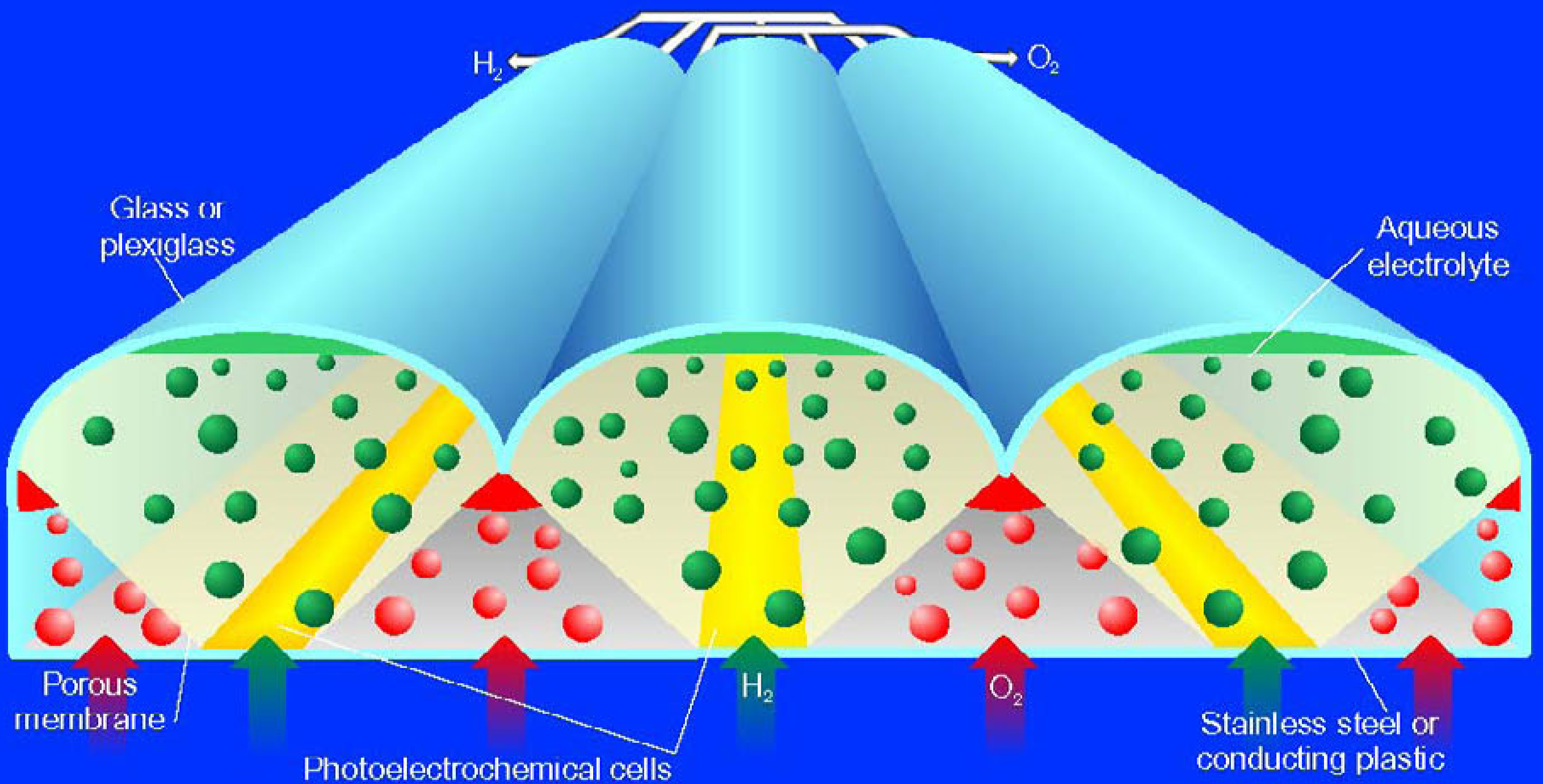
Conclusions

- III-V nitrides
  - Nitride epilayer has enhanced stability
  - Nitrides grown by MOCVD have poor performance in solid state
    - Nitride epilayer limits current (series)
    - Contaminants, nitride traps
    - J_{sc} Maximum 6.4 mA/cm^2
  - PEC water splitting demonstrated on Si-based tandem cell
  - Nitride epilayer needs improvement
- CIGSSe thin films
  - Possible to grow electrodeposited films and do vapor phase enrichment to obtain samples with necessary bandgaps
  - Grading equation develop to predict bandgap-alloy composition relationship.
  - Theoretical high water-splitting efficiency with Si-$CuGaSe_2$ tandem cell.
    - Possible 23% efficiency, but actual tandem cells show very low currents.
    - Electrodeposition of $CuGaSe_2$ on Si PV cell may eliminate problems with high temperature vapor-phase deposition
- SiN thin films
  - n-type and p-type behavior (compensated)
  - Amorphous films produced with a bandgap of 1.9eV
  - Photoresponse enhanced in acidic solution
  - Indications are that the films are stable in aqueous solution
  - Initial results are promising

Conceptual Design of a Photoelectrochemical Water Splitting System with Light Concentration



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What might a panel look like if we discover the right material?

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Responses to Previous Year Reviewers' Comments

- Specific recommendations and additions or deletions to the work scope
  - Very good progress, but industrial partner involvement and more emphasis on computation techniques might have resulted in more progress.
    - Funding of the collaborative projects has been an issue.
- Weaknesses
  - Too many Slides in too little time
    - Poster provides leisurely viewing
  - Limiting internal computational activity continues to be a leading weakness of this project.
    - Agreed! Collaboration with NREL's Computational Sciences Center will continue to be a priority.
    - Others to be added as funding allows.

Future Plans

- Remainder of FY2006:
  - Continue understanding and improvement of nitride-based material: III-V nitrides and SiN.
  - Develop new electrosynthesis approaches and low temperature annealing processes for CIGSSe films.
  - Improve tandem cell design with thin-film CIGSSe.

- For FY2007:
  - Look at possible new materials with UNLV, CSM, …
  - Coatings: SiN, SiC, …
  - Multijunction structures

Presentations and Publications

Papers

- A. M. Fernández, N. Dheree, J. A. Turner, A. M. Martínez, L. G. Arriaga and U. Cano, "Photoelectrochemical characterization of the Cu(In,Ga)S_2 thin film prepared by evaporation", *Solar Energy Materials and Solar Cells*, **85**, Pages 251-259 (2005).
- J. Turner, The Sustainable Hydrogen Economy, *Geotimes*, August 2005

Presentations

- Presentation to high school and middle school science teachers (at NREL) on "The Sustainable Hydrogen Economy" as part of NREL Education days.
- Invited talk at Princeton University entitled "Material and Band Edge Engineering Approaches to Photoelectrochemical Water-Splitting." Princeton, NJ
- Invited lecture at the CSIRO New Materials for Renewable Energy Frontier Science Workshop entitled "Photoelectrochemical Water Splitting: Materials and Systems", Melbourne, Australia.
- Invited lecture at the University of New South Wales entitled "The Sustainable Hydrogen Economy", Sydney, Australia.
- Scripps-Howard Fellows in Environmental Journalism (University of Colorado, Boulder) presentation entitled "Sustainable Hydrogen Economy"
- University of Minnesota, presentation entitled "Material and Band Edge Engineering Approaches to Photoelectrochemical Water-Splitting ".
- Invited talk at the Air & Waste Management Association 97th Annual Conference entitled "The Sustainable Hydrogen Economy" in a session entitled "Is the Hydrogen Economy Sustainable?"
- Invited talk at the 2005 Colorado Renewable Energy Conference presentation entitled "The Sustainable Hydrogen Economy".
- Talk on Hydrogen and Fuel Cells to middle and high school teachers as part of NRELs PPRISM Professional Development Day.
- Invited talk at Fermilab (Chicago) entitled "The Sustainable Hydrogen Economy".
- Presentation as part of the NREL 2005 Summer Intern Program, entitled "Hydrogen and Fuel Cells".
- Kansas Energy Council, presentation entitled "Hydrogen Production and Fuel Cells".
- Presentation to Institute of Nuclear Energy Research (Taiwan), entitled "Fuel Cell Research and H_2 from Photoelectrochemical Systems"
- American Scientific Affiliation annual meeting, presentation entitled " Fuel Cell Technology and the Sustainable Hydrogen Economy "
- Invited talk at the 2005 Solar World Congress entitled "The Sustainable Hydrogen Economy" in a forum entitled "Renewable Fuels and Other Options to Reduce World Oil Consumption".
- Presentation to Fort Carson (Colorado) Sustainability group, entitled "Hydrogen and Fuel Cells".
- Denver Area Physics Teachers, presentation entitled "Fuel Cells and the Hydrogen Economy".
- Department of Metallurgical and Materials Engineering, Colorado School of Mines, research seminar, presentation entitled "Photoelectrochemical Water-Splitting: Materials and Systems".

Presentations (2)

- Presentation to the University of Georgia's College of Agriculture and Environmental Sciences, the National Environmentally Sound Production Agriculture Laboratory, and representatives from the Georgia State Government and Georgia agricultural industry, entitled "Sustainable Hydrogen"
- Lecture for Colorado School of Mines, Fuel Cell class entitled "The Sustainable Hydrogen Economy".
- "Photoelectrochemical Hydrogen Production", International Partnership for Hydrogen Energy, Renewable Hydrogen Workshop. Seville, Spain.
- "Direct Photoelectrochemical Production of Hydrogen", Instituto de Ciencia de Materiales de Barcelona, Barcelona, Spain
- "Water Photolysis for the Production of Hydrogen" CeRMAE Energy Challenges, Barcelona Spain.
- "Photoelectrochemical Water-Splitting: Materials and Systems", Department of Materials Science and Engineering, Rensselaer Polytechnic Institute.
- Dr. Todd Deutsch, Contributed Talk, "Renewable hydrogen: Direct conversion of photons to fuel on III-V nitrides", Pacifichem
- Dr. Jennifer Leisch, Contributed Talk, "CuGaSe2/Si Tandem Devices for Photoelectrochemical Water Splitting", 208th Meeting of the Electrochemical Society, Los Angeles, CA, October 17, 2005
- Dr. Jennifer Leisch, Educational Outreach, Presentation and Demonstration on Renewable Energy, Pomona High School, Arvada, CO. February 1, 2006. Organizing Teacher: Robert Pizem, Earth Sciences Department
- Dr. Jennifer Leisch, Contributed Talk, "CuGaSe2/Si Tandem Electrodes for Photoelectrochemical Hydrogen Production" Western States Catalysis Club Symposium, Boulder, CO, February 24, 2006
- Dr. Jennifer Leisch, Contributed Talk, "CuInSe2 and Related Alloys for Photoelectrochemical Hydrogen Production", Department of Chemistry Seminar Series, Colorado School of Mines, February 28, 2006
- Dr. Jennifer Leisch, Keynote Talk, " CuInSe2 Materials for Photoelectrochemical Hydrogen Production", 1st Annual Symposium on Hydrogen from Renewable Sources and Refinery Applications, 231st Meeting of the American Chemical Society, Atlanta, GA, 27 March 2006
- Dr. Jennifer Leisch, Contributed Talk, "CIS-based Thin Films from Electrodeposited Precursors for Photoelectrochemical Hydrogen Production", 209th Meeting of the Electrochemical Society, Denver, CO, May 8, 2006
- "Addressing the Challenges Ahead: The Sustainable Hydrogen Economy", The Colorado Renewable Energy Society.
- "Hydrogen and Fuel Cell Technology", to Connecticut Clean Energy Fund.
- "Addressing the Challenges Ahead: The Sustainable Hydrogen Economy" to Schlumberger Carbon Services.
- "Photoelectrochemical Water-Splitting:Materials and Systems", Department of Chemistry, University of Nevada Las Vegas
- "Materials and Systems for Photoelectrochemical Water-Splitting", Department of Chemical & Metallurgical Engineering, University of Nevada Reno

Project Safety

- Hydrogen generation from our samples is small (a few μl/min), so no special precautions over standard engineering controls for chemical laboratories are taken at this time.
  - Sample sizes are small (<0.5 cm^2) so hydrogen production even from the most efficient cells is low.
  - Cells are open to allow rapid diffusion of the hydrogen (no build-up).
  - Air exchanges are 6-10/hour in the lab.
  - For PEC H_2 and O_2 are produced at separated electrodes.
- For scale-up, a complete hazard identification and risk assessment will be done to identify issues relating to personnel, equipment and environmental factors.
  - Hardware and material analysis will be done to identify possible component failure modes.
  - This will be integrated into the design of the test facility and modules, and guide the write-up of the operational procedures.