

Photoelectrochemical Water Systems for H₂ Production

2006 DOE Hydrogen, Fuel Cells and Infrastructure
Technologies Program Review

May 16, 2006

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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

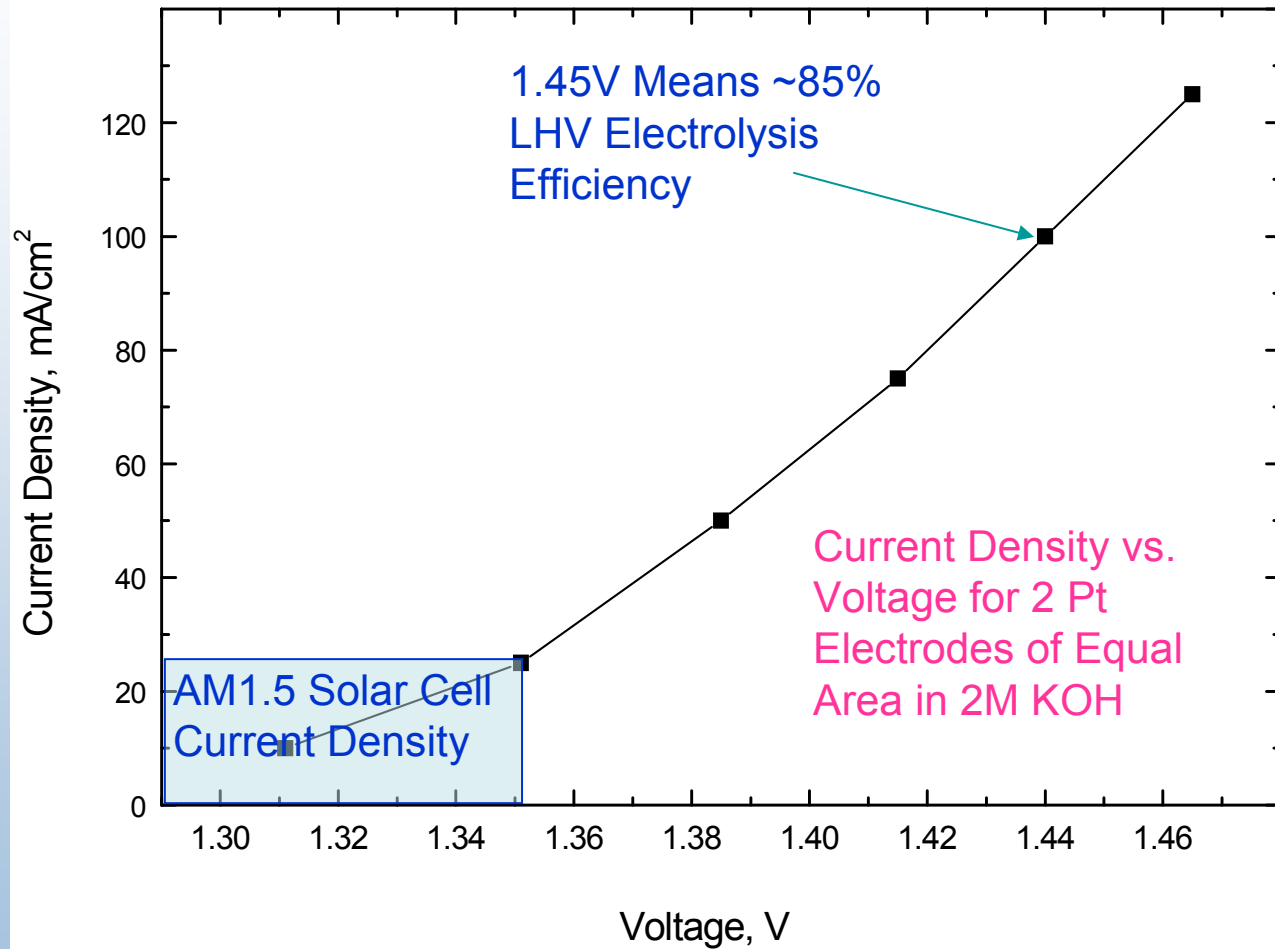
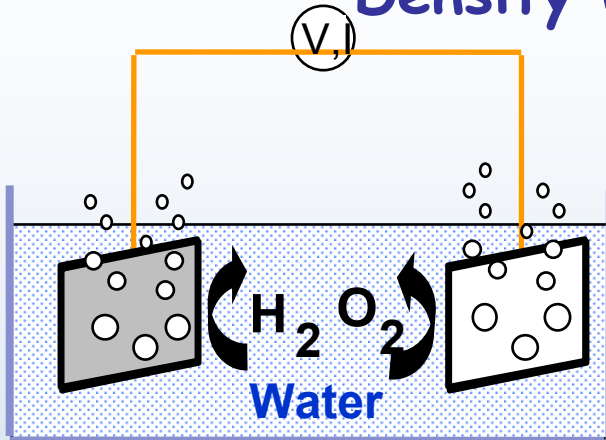
Photoelectrochemical Conversion

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.

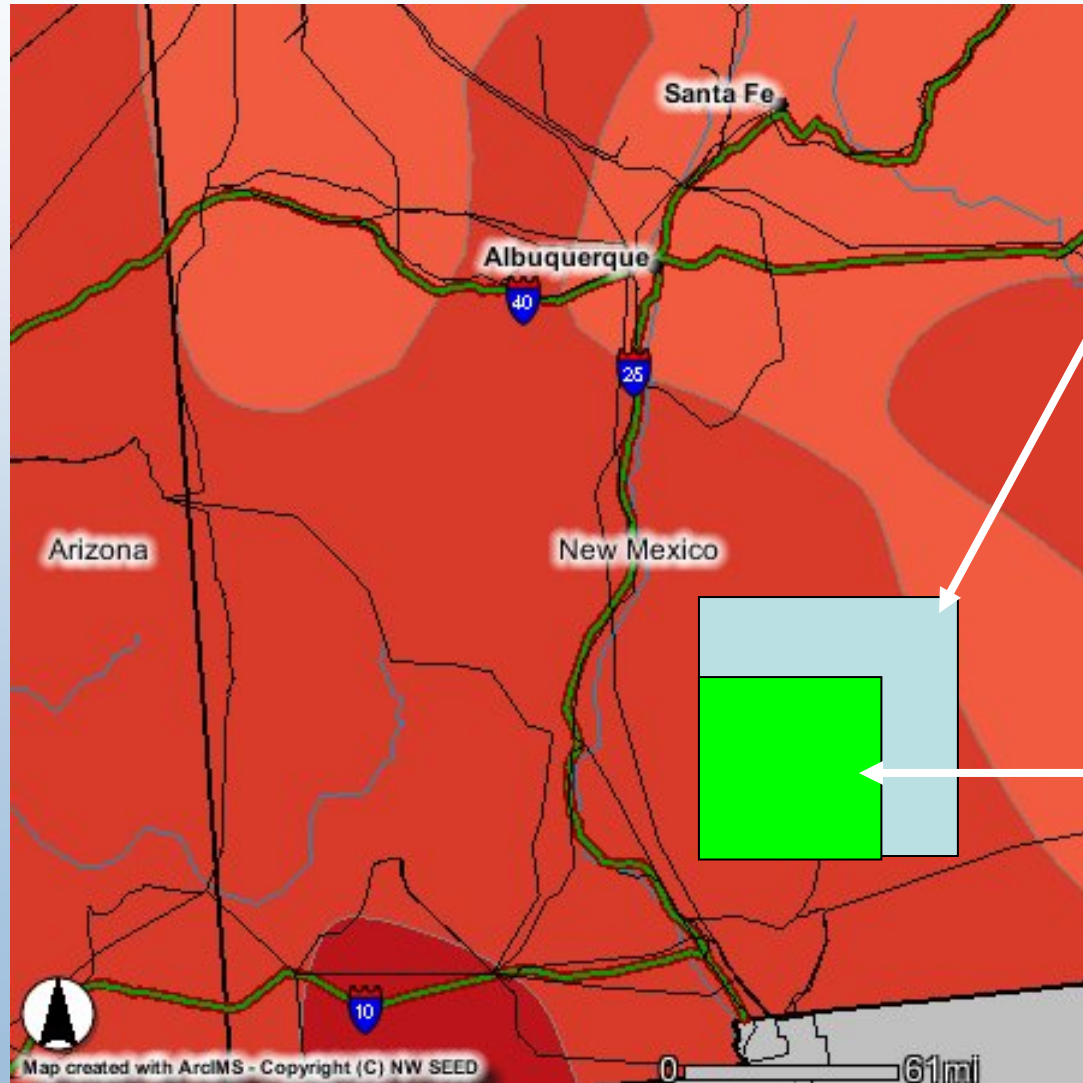
Higher Efficiency from PEC Devices (as Compared to PV/Electrolysis) Stems from the Lower Operational Current Density when using Direct Solar Light



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

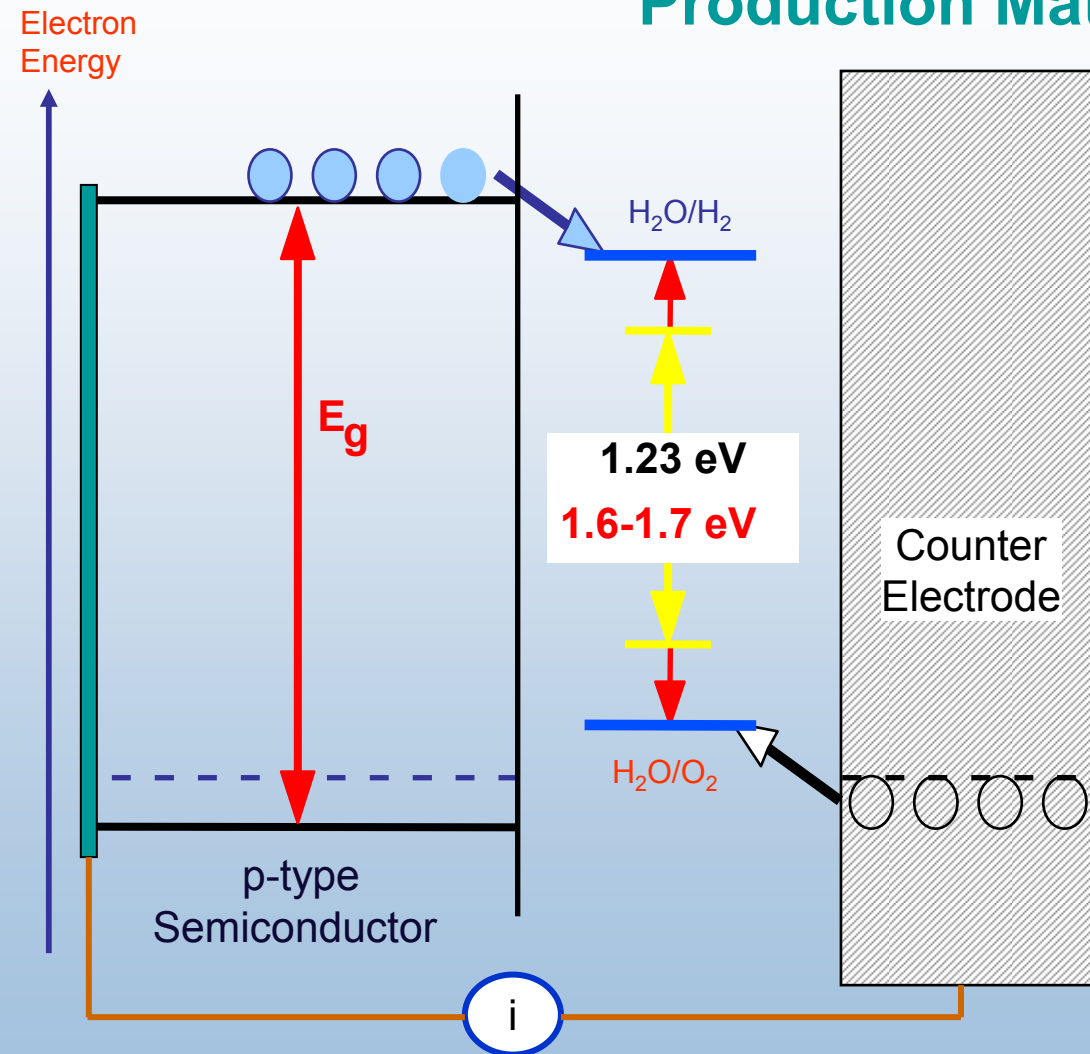


PV panel area to produce hydrogen for current U.S. fleet (10% system, 70% electrolysis efficiency)

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

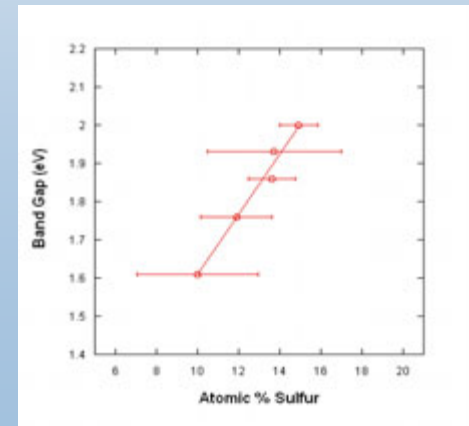
➤ **Energetics** – the band edges must straddle H_2O redox potentials (**Grand Challenge**)

All must be satisfied simultaneously

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**:

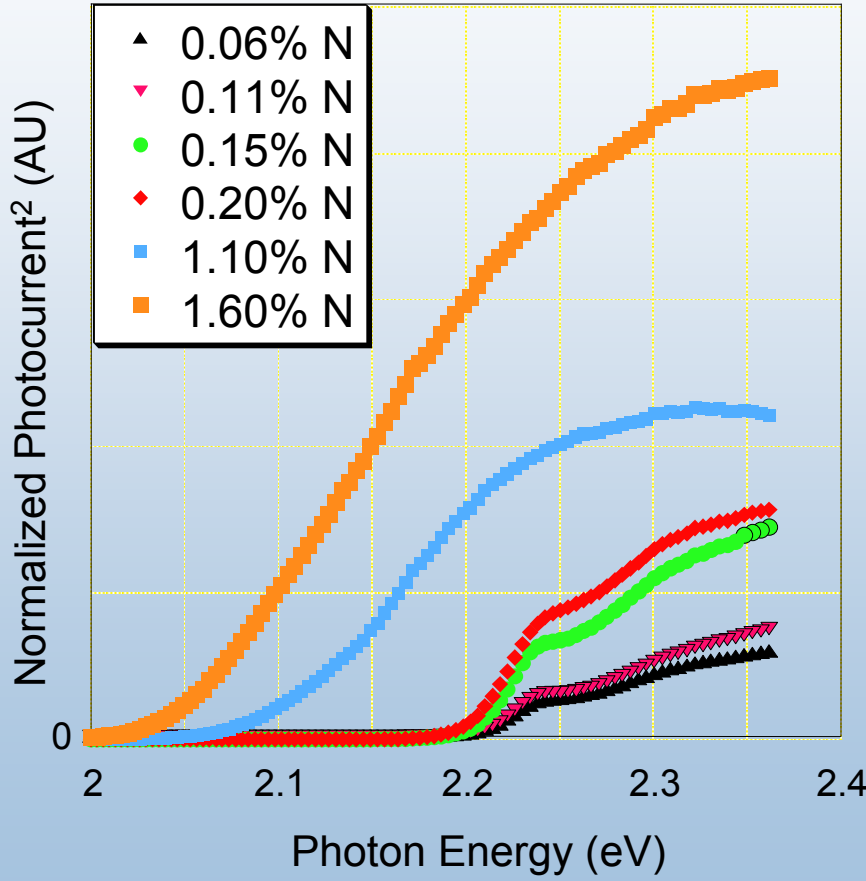
- *GaPN - NREL (high efficiency, stability)*
- *CuInGa(Se,S)₂ - UNAM (Mexico), NREL (low cost)*
- *Silicon Nitride - NREL (protective coating, new material)*
- *GaInP₂ - NREL (fundamental materials understanding)*
- Energetics
 - Band edge control
 - Catalysis
 - Surface studies



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

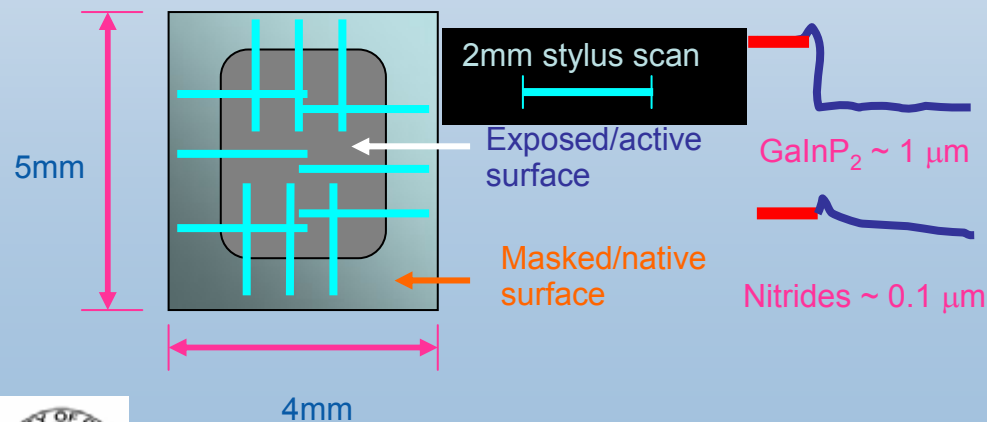
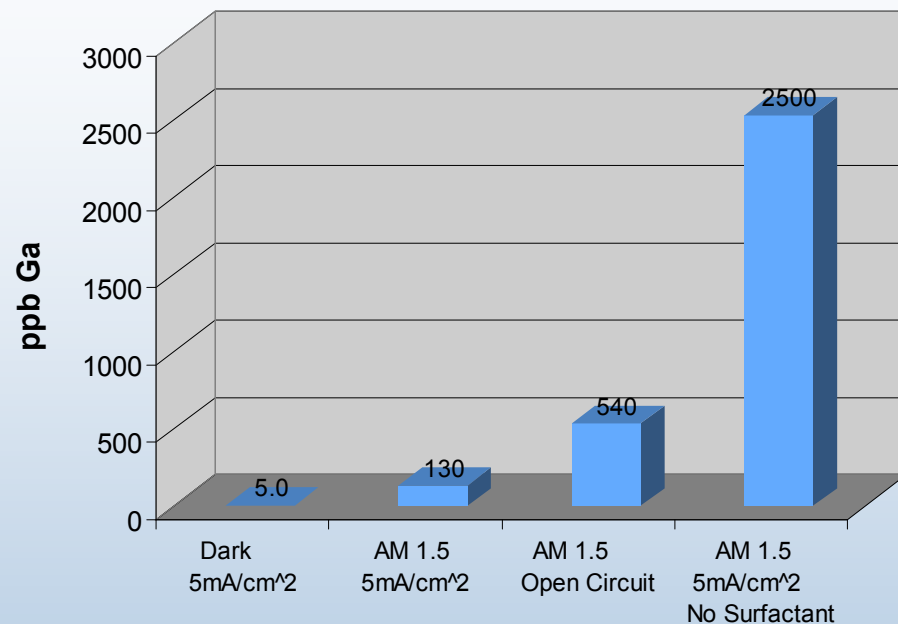
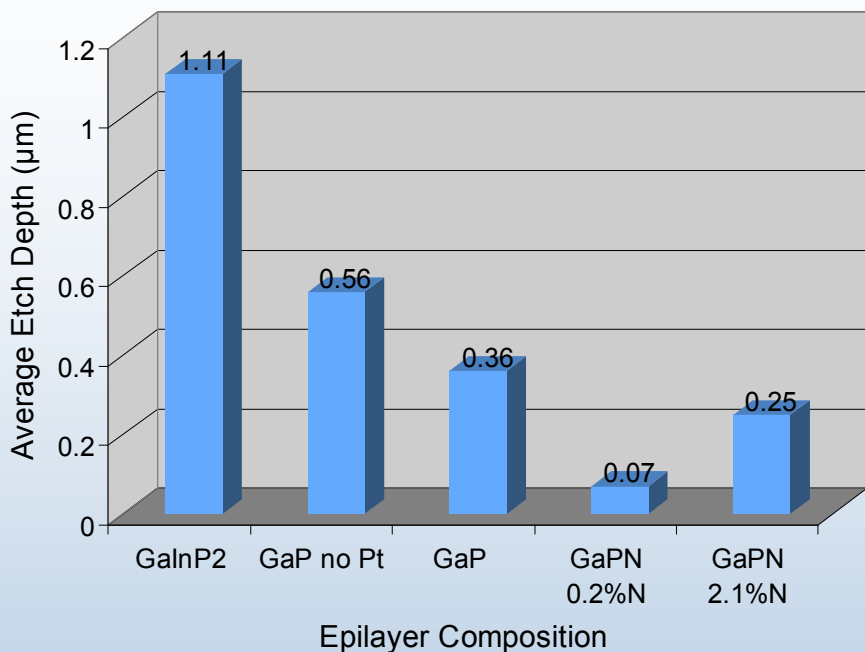
GaP_{1-x}N_x Epilayer Direct Band Gap



Dr. Todd Deutsch



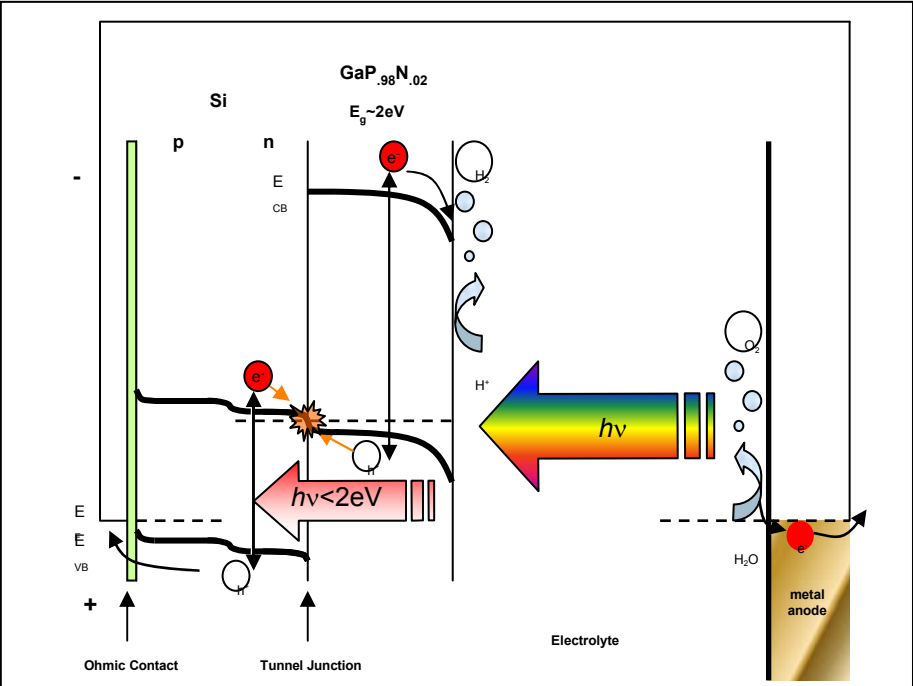
GaPN Stability Measured by Profilometry and by ICP-MS of Solution



- Photocathode durability testing
 - 5mA/cm², AM 1.5, 24 hours, 3M H₂SO₄, pulsed Pt treatment
 - Ga content of solutions by ICP-MS
 - Etching by profilometry
- Represents ~300 hrs of stability for 1 μm layer

GaPN:Si Tandem Cell

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



Direct Eg (eV)
Nitrogen%

1 μ m p-GaP _{0.98} N _{0.02}
0.15 μ m p+ GaP
0.7 μ m n+ GaPN
0.04 μ m GaP buffer
0.2 μ m n-Si (P diff)
p-Si Substrate
Al Ohmic contact

Tunnel Junction

20mm

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%

25mm

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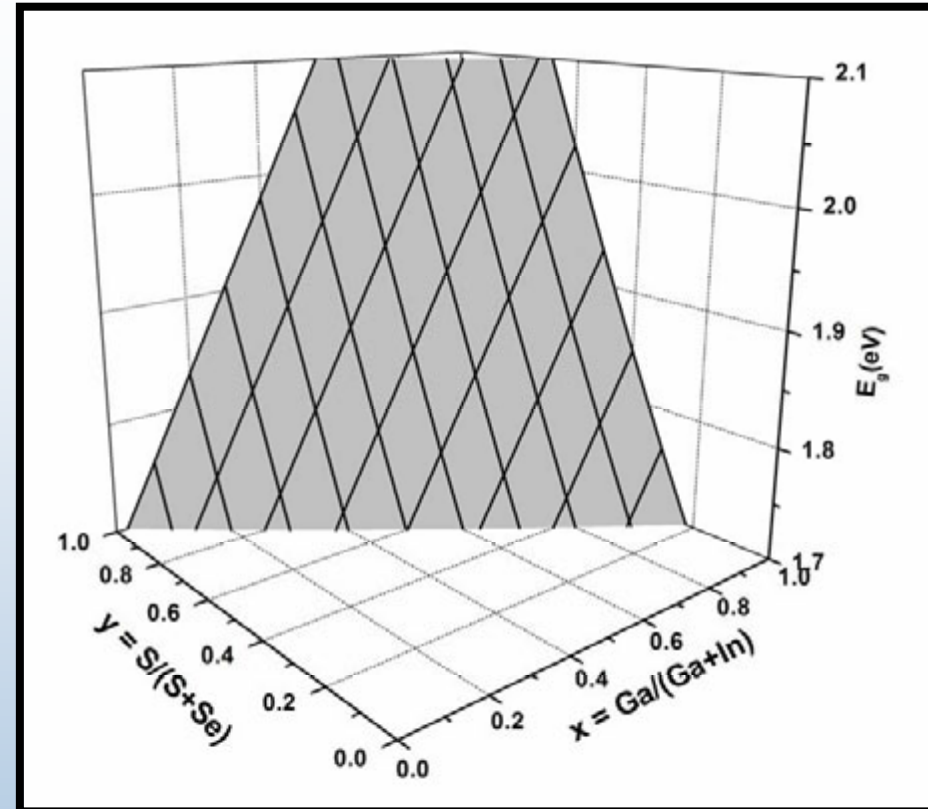


Electrodeposited CIGSS

- CIS material system: $\text{CuInSe}_2 - \text{CuGaS}_2$
 - E_g range: 1.0 – 2.5eV
- CuGaSe_2 : $E_g = \sim 1.7$
- High PV efficiencies in this system
- Potential low cost, low energy deposition
- Two configurations:
 - Single materials
 - As a layer in a multijunction system



Dr. Jennifer E. Leisch

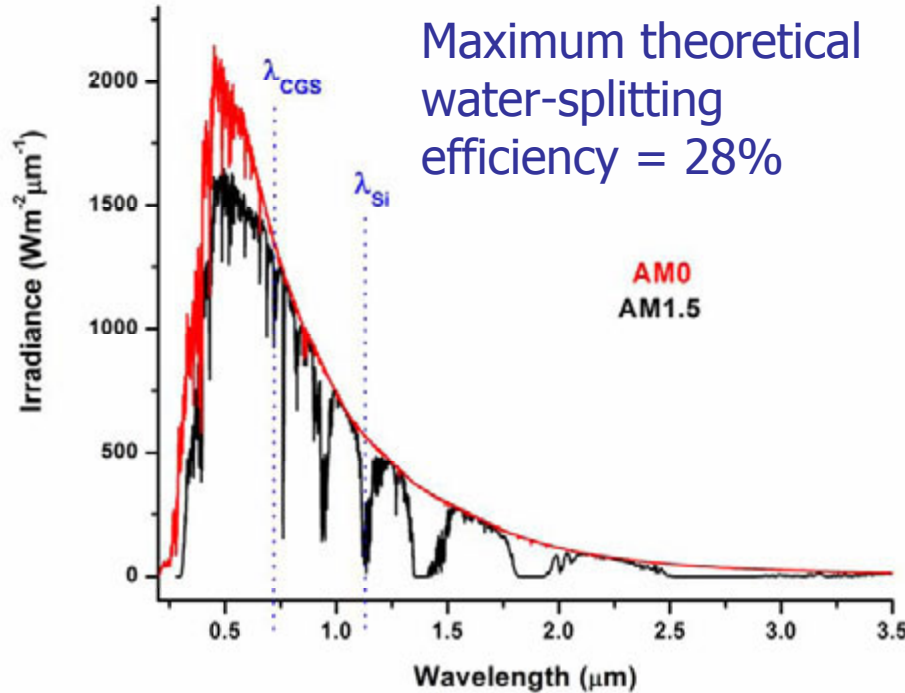
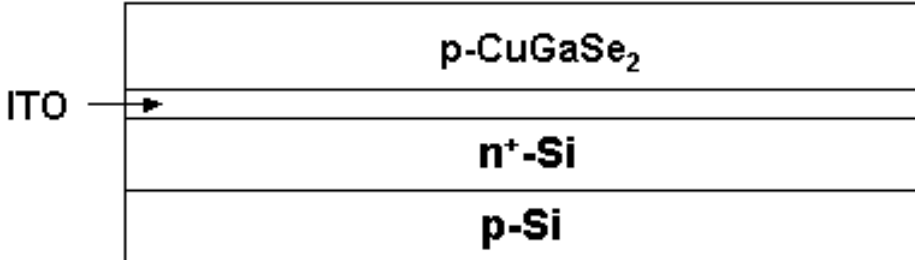


Relationship of bandgap to alloy composition. Gray area represents compositions that produce bandgaps in the range 1.7 - 2.1eV

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

Tandem Cell Configuration

CGS Grown by Thermal Evaporation



Maximum theoretical water-splitting efficiency = 28%

CGS: 1.3μm
ITO: 150nm



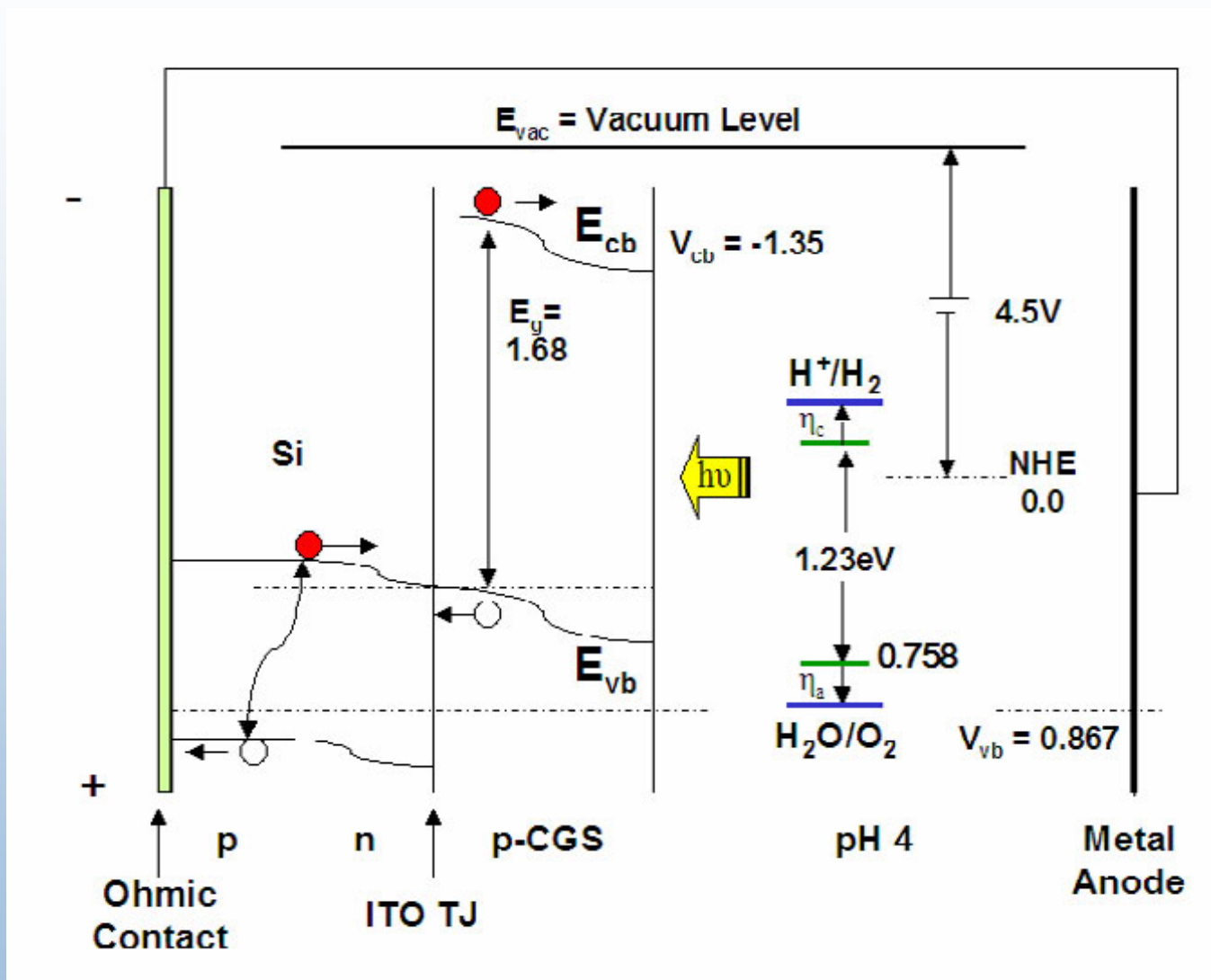
Dr. Jennifer E. Leisch

Results – Band Energy Diagram

Energetics say:
 H₂O splitting, but
 very low currents

Why?

- Poor ITO TJ
- Kinetics for H₂
- Recombination
- Band shifting
- Corrosion



Results – Stability

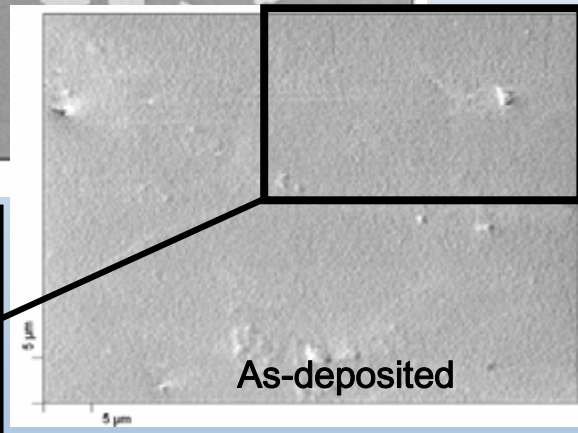
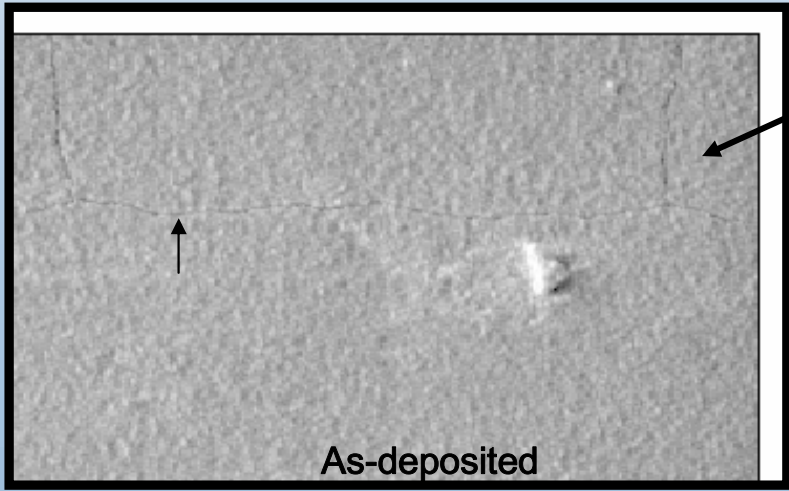
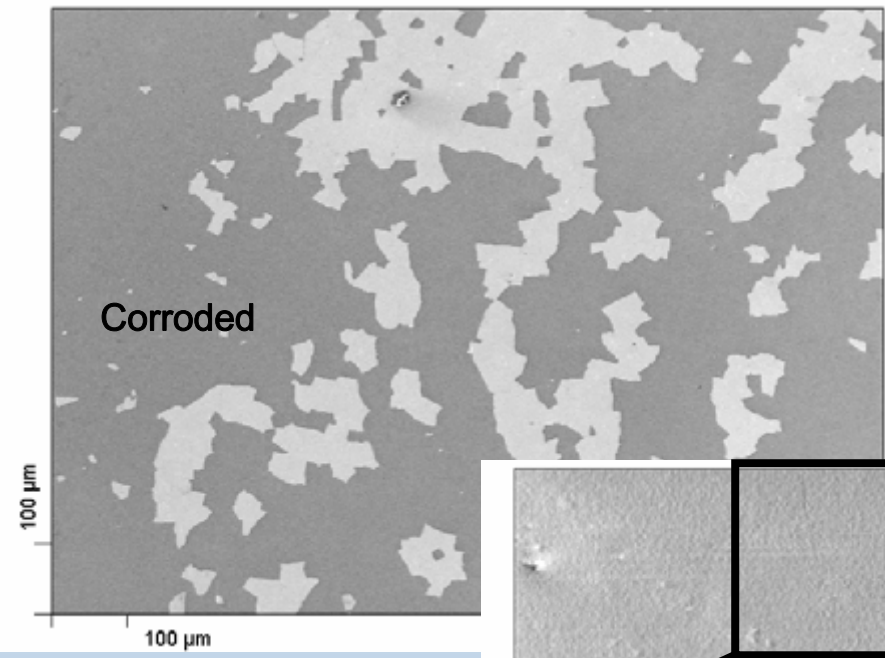
Visible cracks lead to undercutting of the CGS layer.

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.

2mA/cm², 3M H₂SO₄,
2hrs.
100mW/cm² W
Illumination
.03mL/min-cm² H₂
evolution

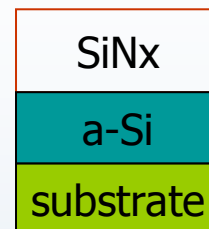


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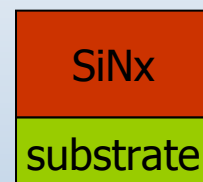


Thin-Film Silicon Nitride for PEC Devices

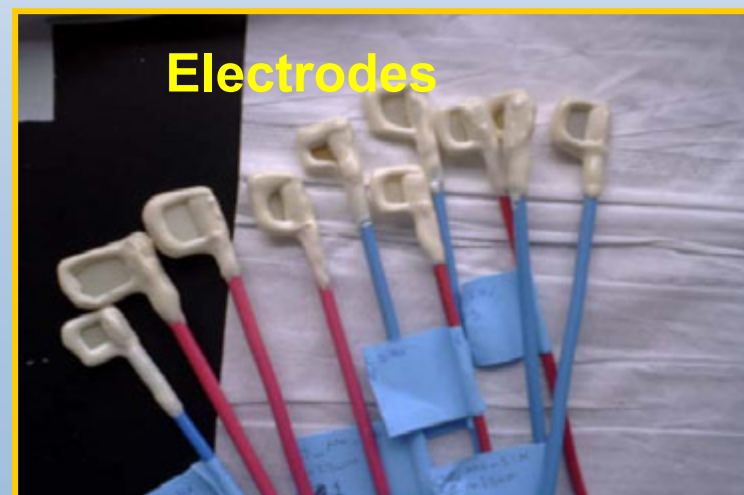
- Known stable material
- Synthesis conditions can produce transparent and nontransparent films, possibilities of:
 - Corrosion resistant transparent coating
 - Direct water splitting system as a single device or as part of a tandem
- Low cost, high volume synthesis possibilities



Corrosion Protection



Water-splitting



Thin Film Silicon Nitride from DC Magnetron Sputtering

Sputter Silicon Target in Nitrogen Atmosphere

200 W

N₂ added to 4.5mTorr

Argon: 0 to 10.0 sccm

Room temperature

Si target

5" gun-substrate

ITO on glass

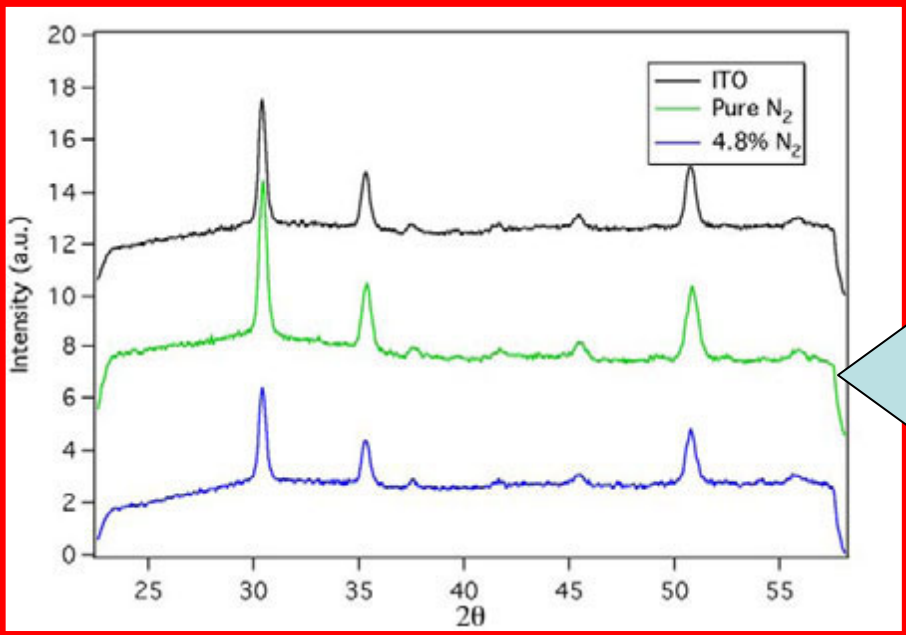
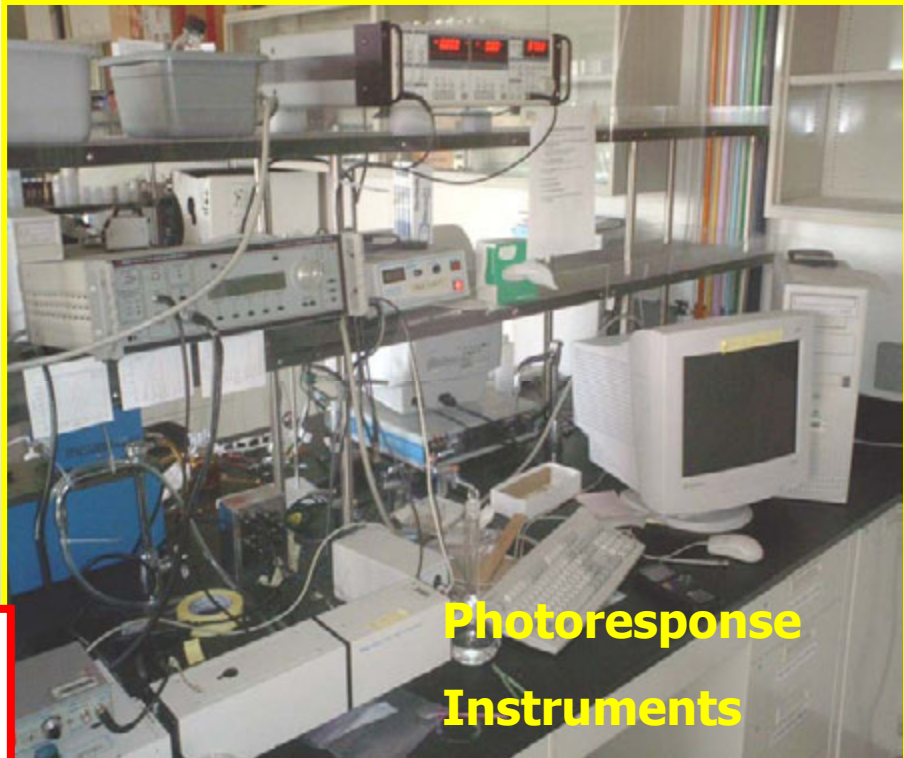
10.0 sccm

4.8 %
N₂

0 sccm
Pure N₂

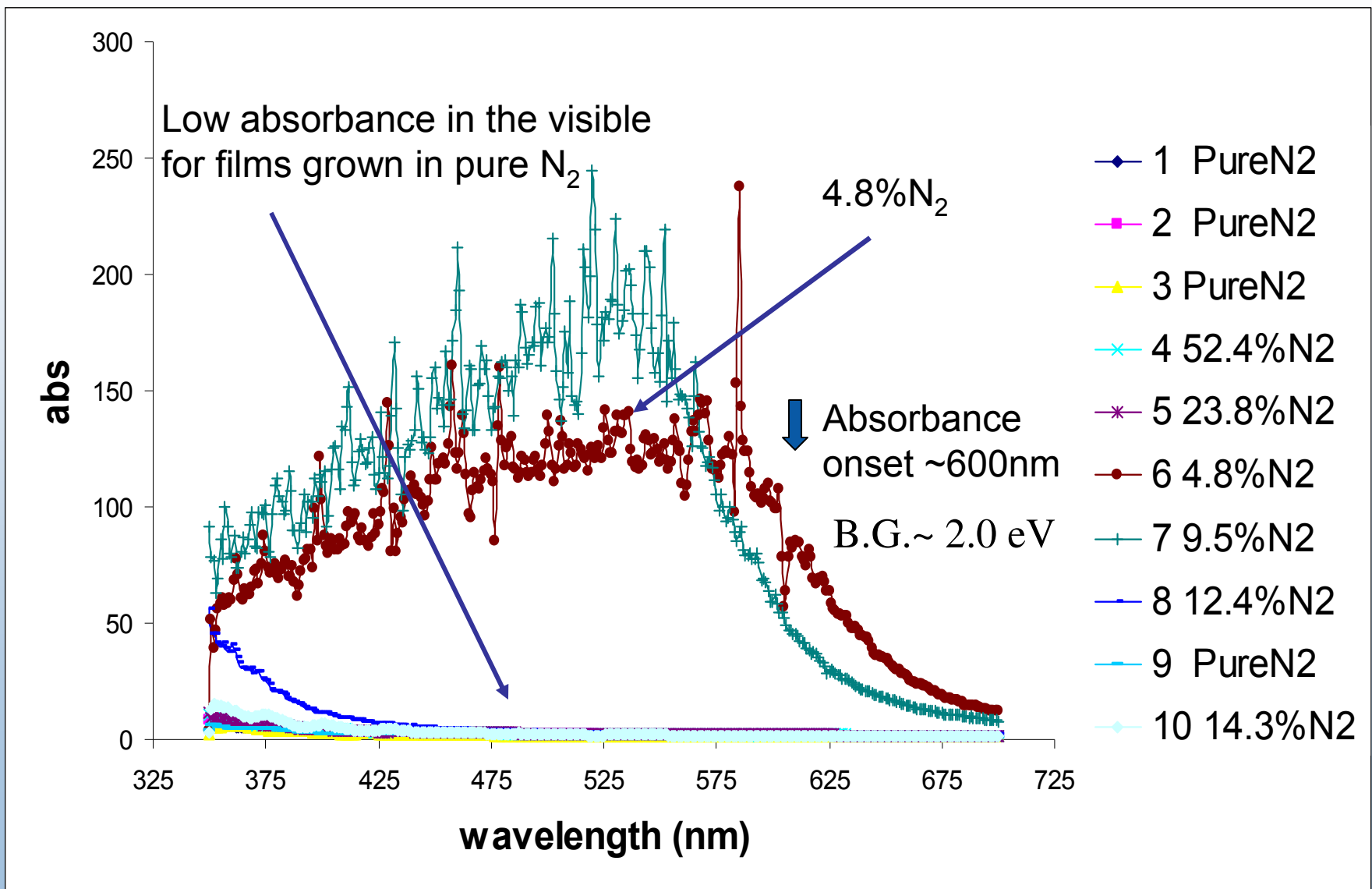
Analysis Techniques

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

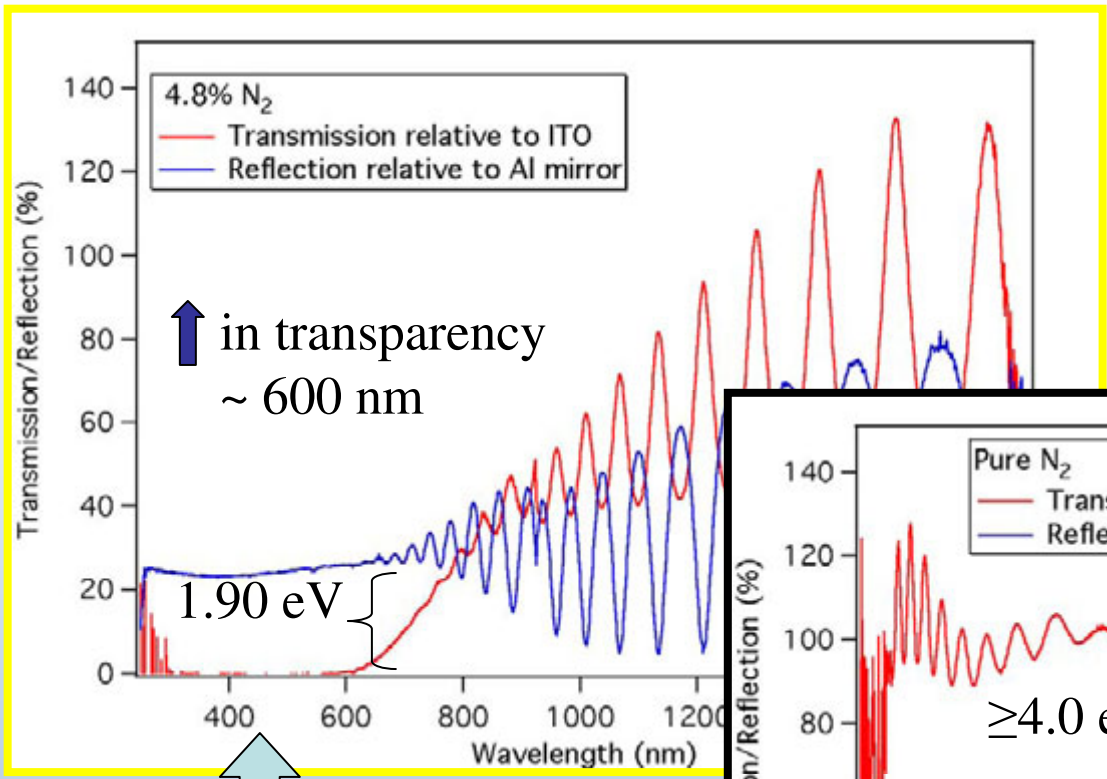


X-ray diffraction measurements indicate that the films are amorphous

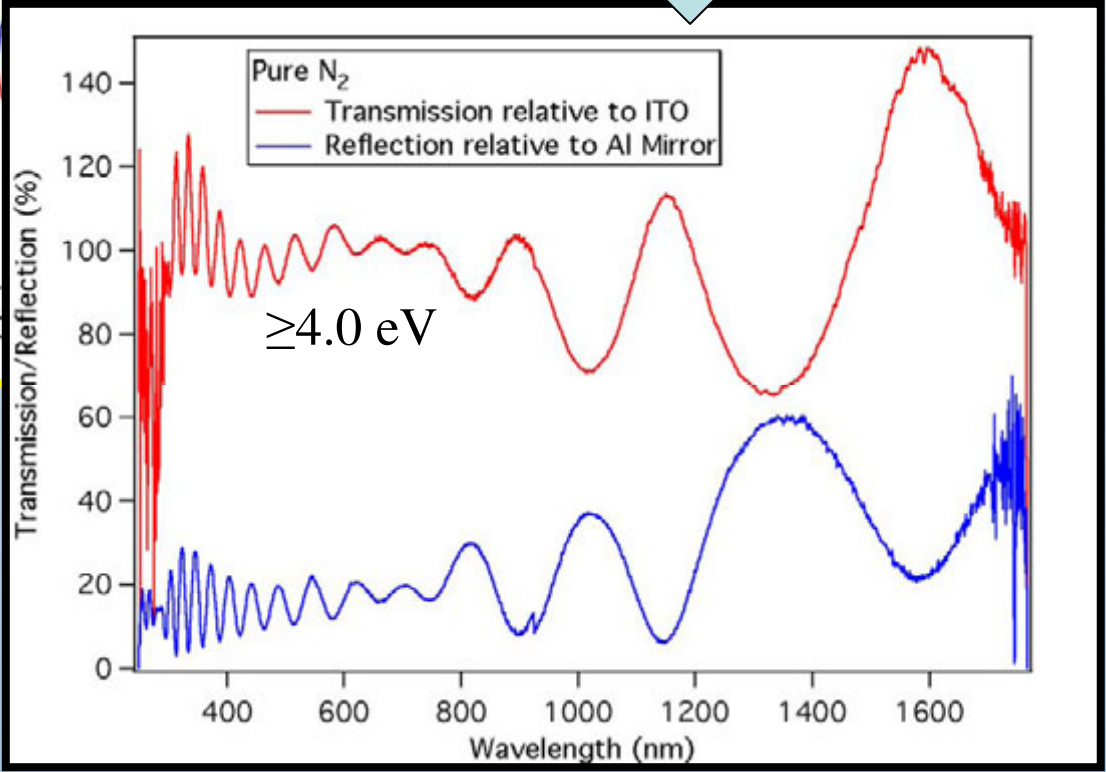
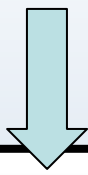
Initial Absorbance Measurements



Optical Transmission/Reflection



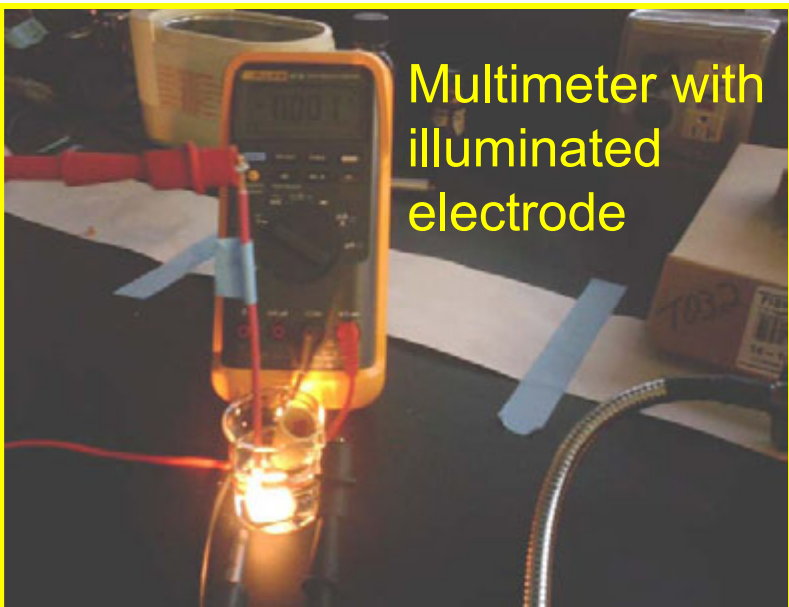
High transparency for films grown in pure nitrogen



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

Photo-Effects for As-Grown SiN

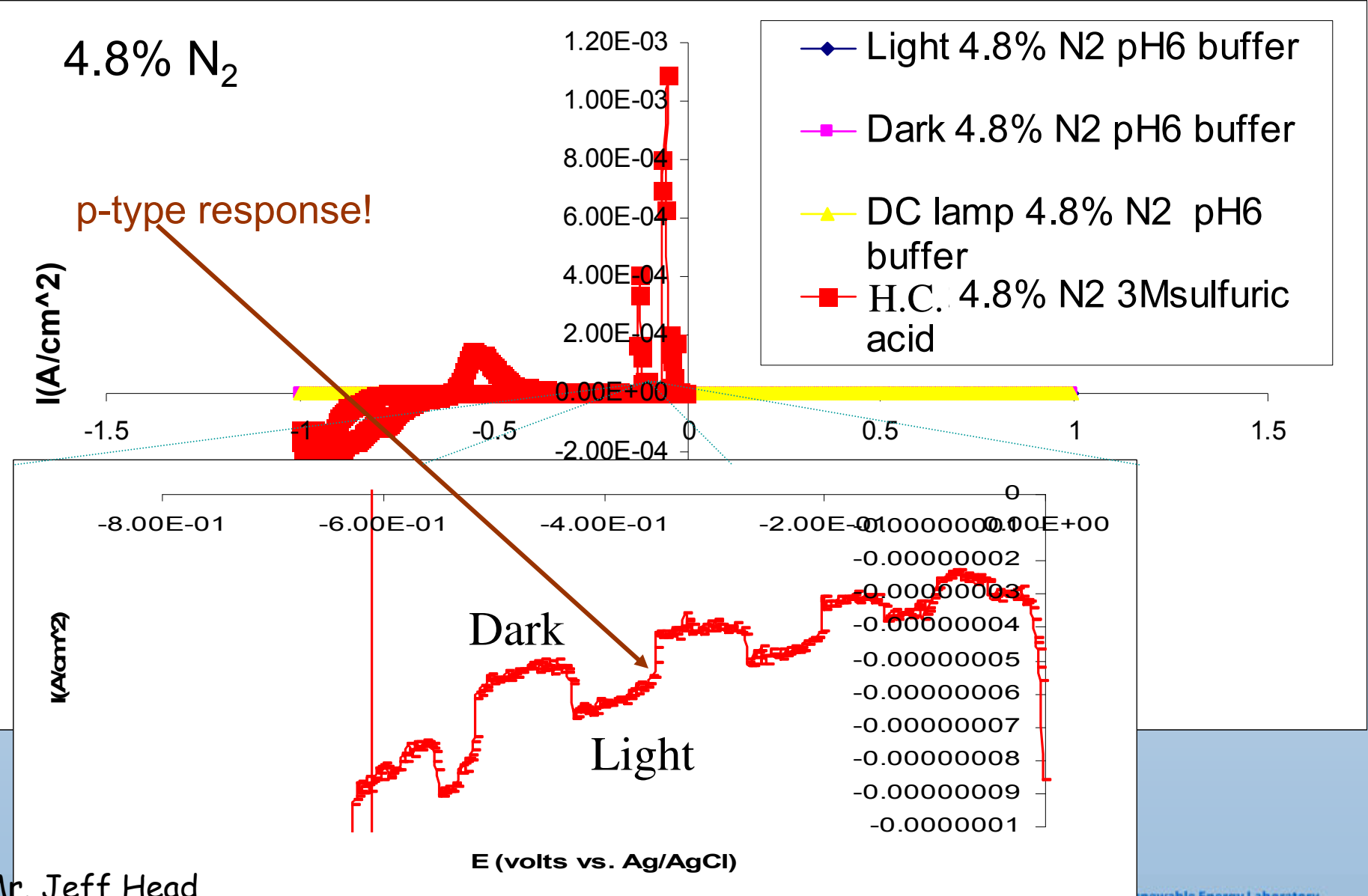
- Films grown in pure nitrogen show very little photoeffect (transparent)
- Film grown in 4.8% N₂ shows largest $\Delta V = -131\text{mV}$
- n-type response
- Four point conductivity $\geq 10^7 \Omega/\text{square}$



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

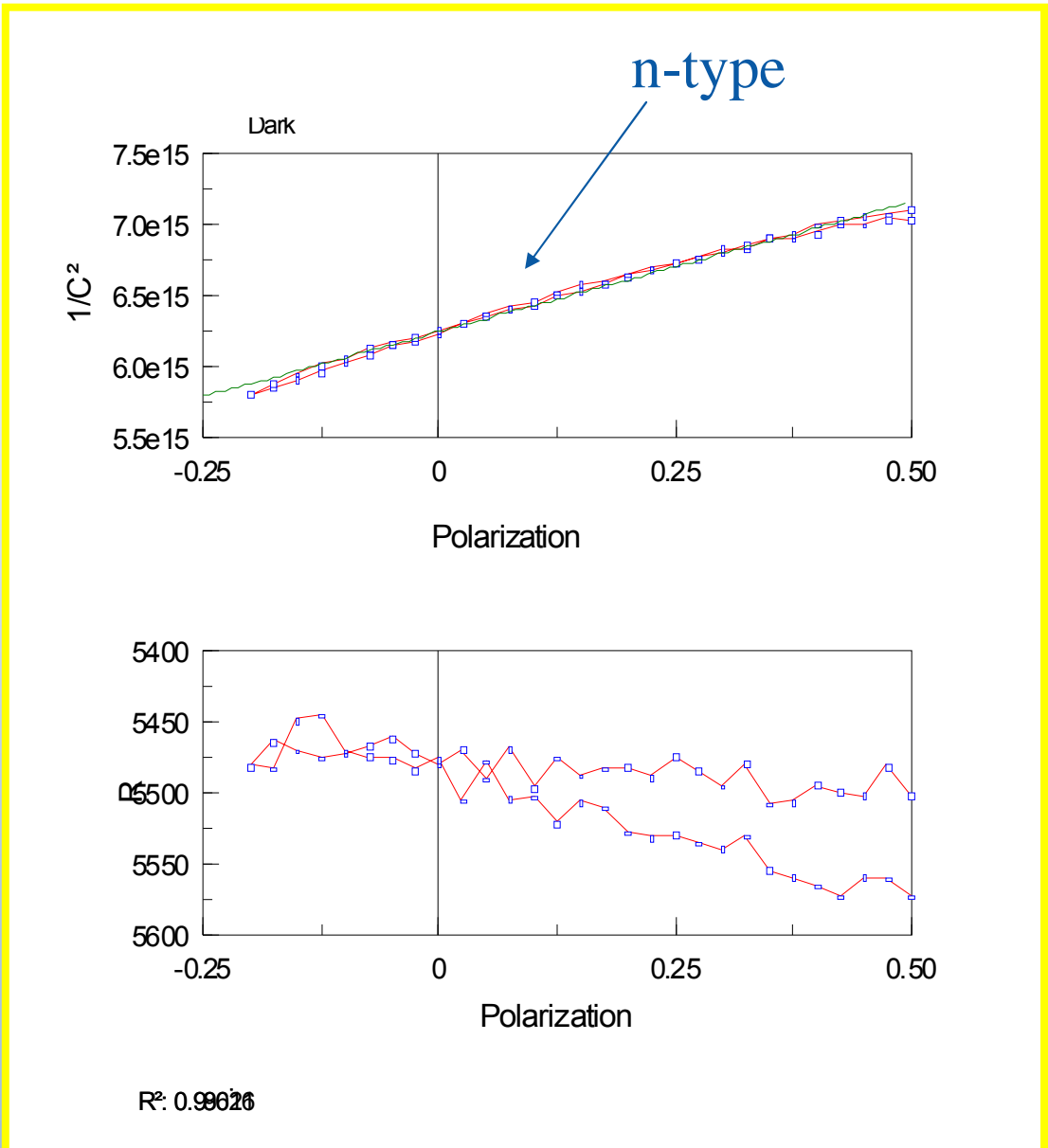
Photocurrent Measurements

Shows a p-type Response in Acid

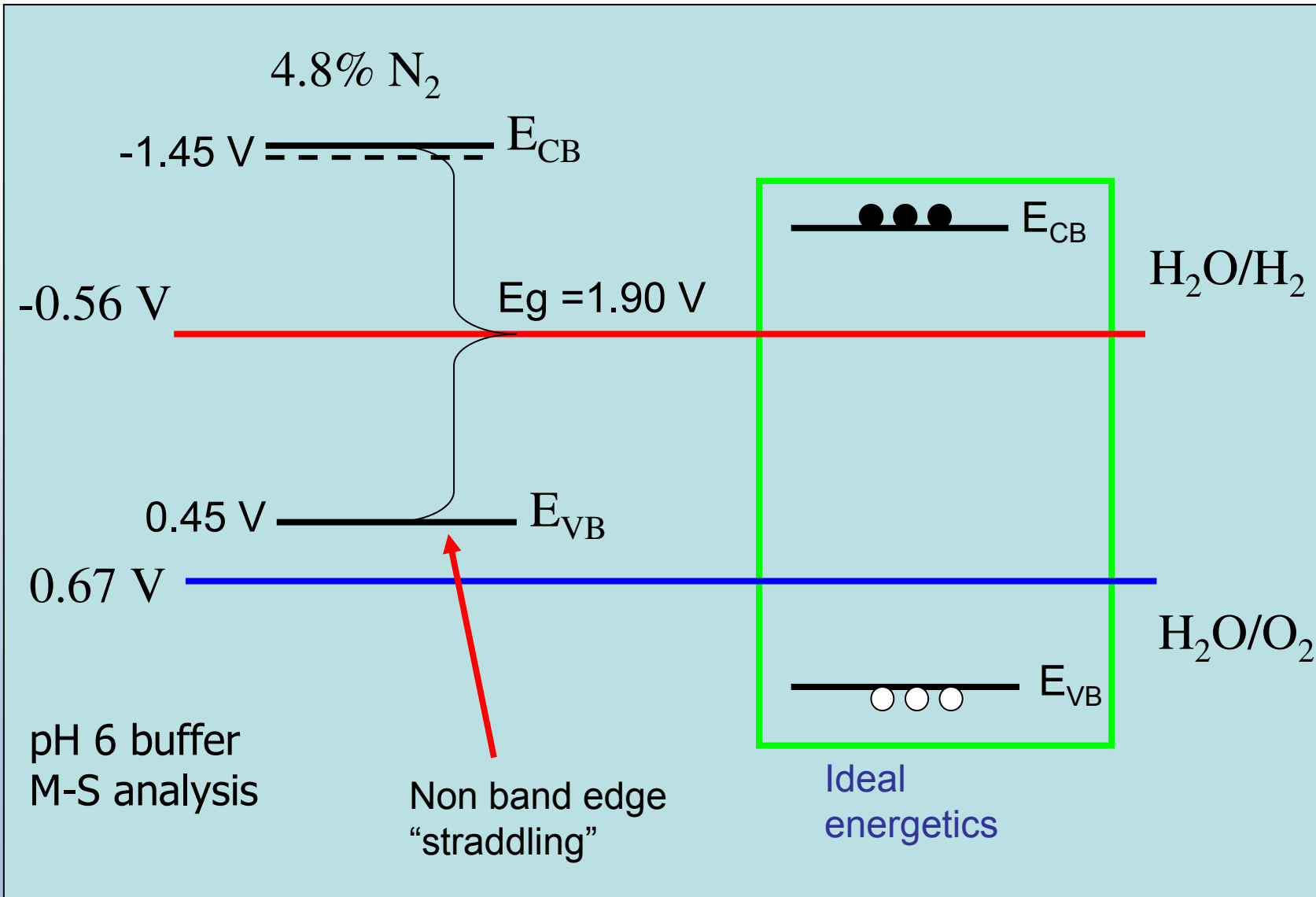


Mott-Schottky Analysis

- Slope indicates n-type semiconductor
 - 4.8% N₂ = -1.45 Vfb
 - significant variation between samples
- Doping density ranges between 10¹⁵ to 10¹⁷/cm³
- Material is probably highly compensated, which gives rise to its dual n- and p-type response



Band Edge Positions (Preliminary)



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/cm²
- PEC water splitting demonstrated on Si-based tandem cell
- Nitride epilayer needs improvement

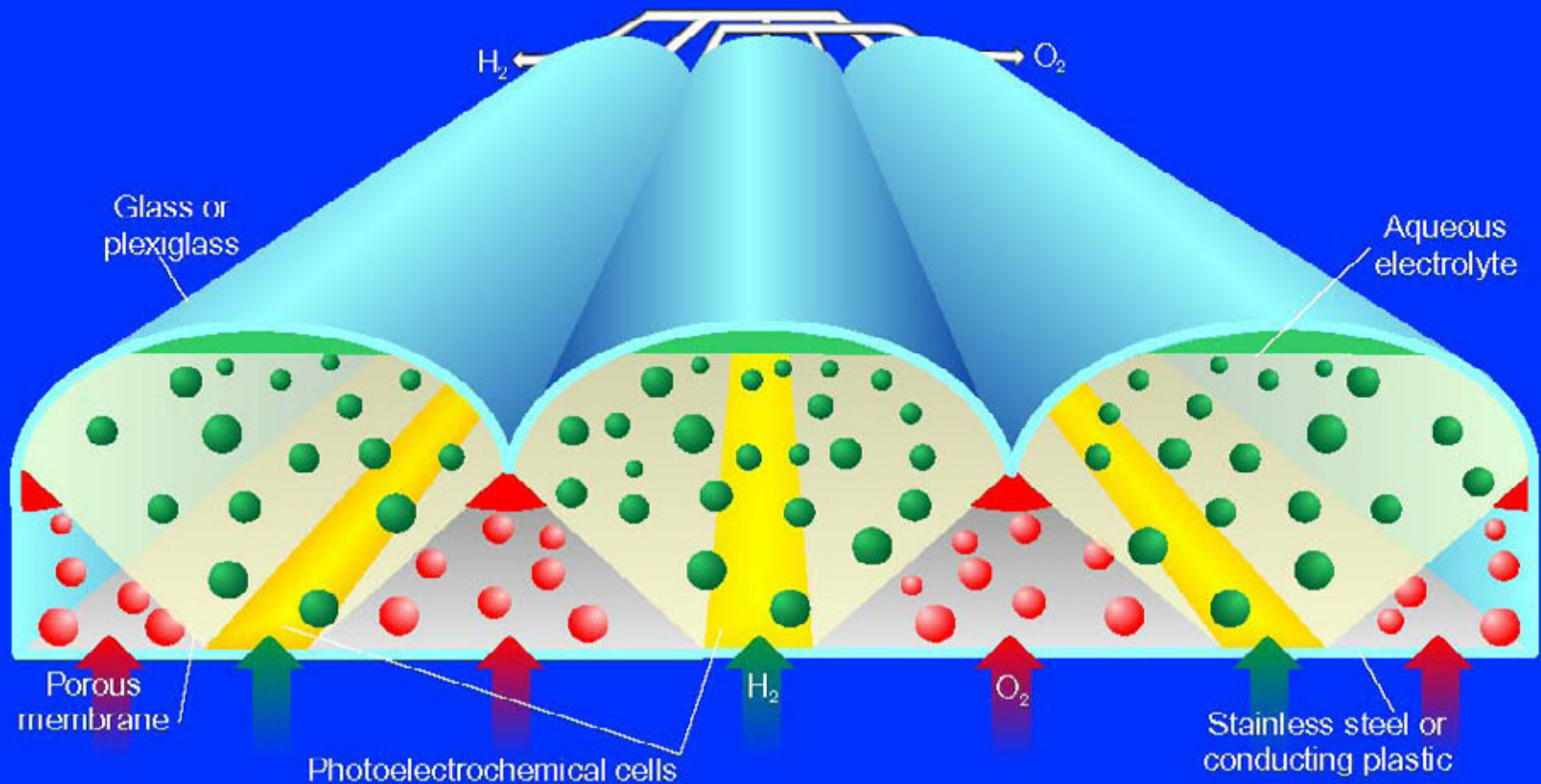
- CIGSSe thin films

- 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-CuGaSe₂ tandem cell
 - Possible 23% efficiency, but actual tandem cells show very low currents
 - Electrodeposition of CuGaSe₂ 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



1995

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

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)S₂ 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
- 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 NREL's PPRISM Professional Development Day
- Invited talk at Fermilab (Chicago) entitled "The Sustainable Hydrogen Economy"

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 "Is the Hydrogen Economy Sustainable?" session
- 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 H₂ 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" at the "Renewable Fuels and Other Options to Reduce World Oil Consumption" forum
- 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, March 27, 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," Colorado Renewable Energy Society
- "Hydrogen and Fuel Cell Technology," 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 $\mu\text{l}/\text{min}$), so no special precautions over standard engineering controls for chemical laboratories are taken at this time
 - Sample sizes are small ($<0.5 \text{ cm}^2$), 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 will guide the write-up of the operational procedures