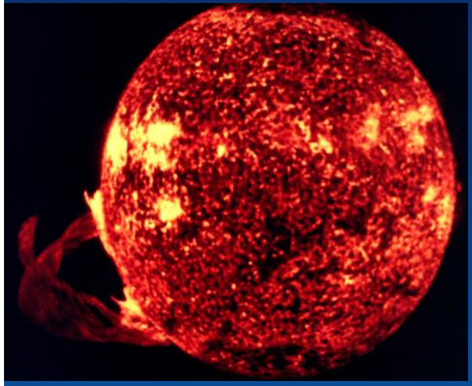
A national laboratory of the U.S. Department of Energy
Office of Energy Efficiency & Renewable Energy

NREL National Renewable Energy Laboratory

Innovation for Our Energy Future

Semiconductor Materials and Tandem Cells for Photoelectrochemical Hydrogen Production: $GaP_{1-x}N_x$ and Cu(In,Ga)Se,S)

ICMR Symposium on Materials Issues in Hydrogen Production and Storage



Santa Barbara, CA

August 24, 2006

John A. Turner

John_Turner@nrel.gov   303-275-4270

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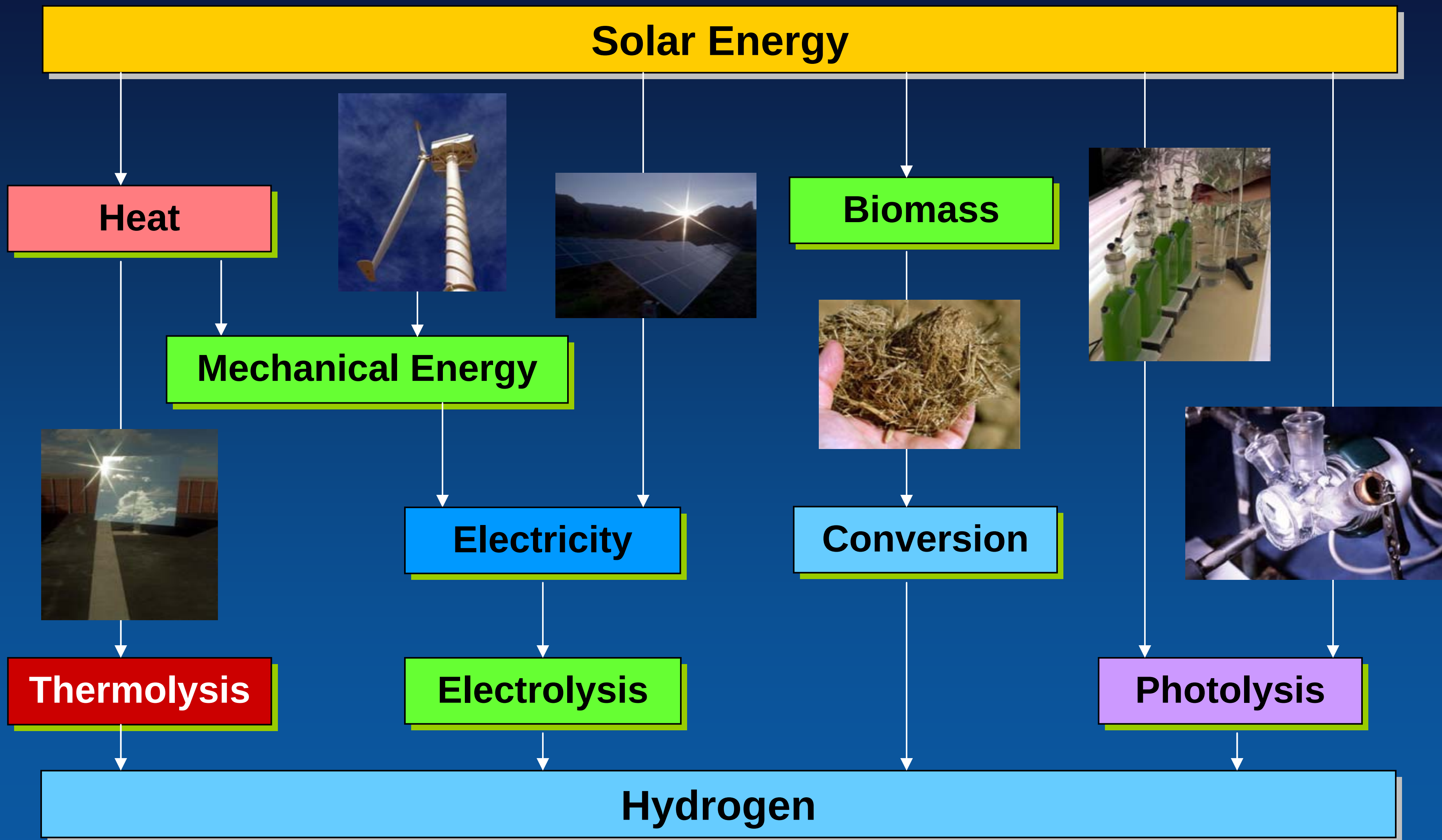
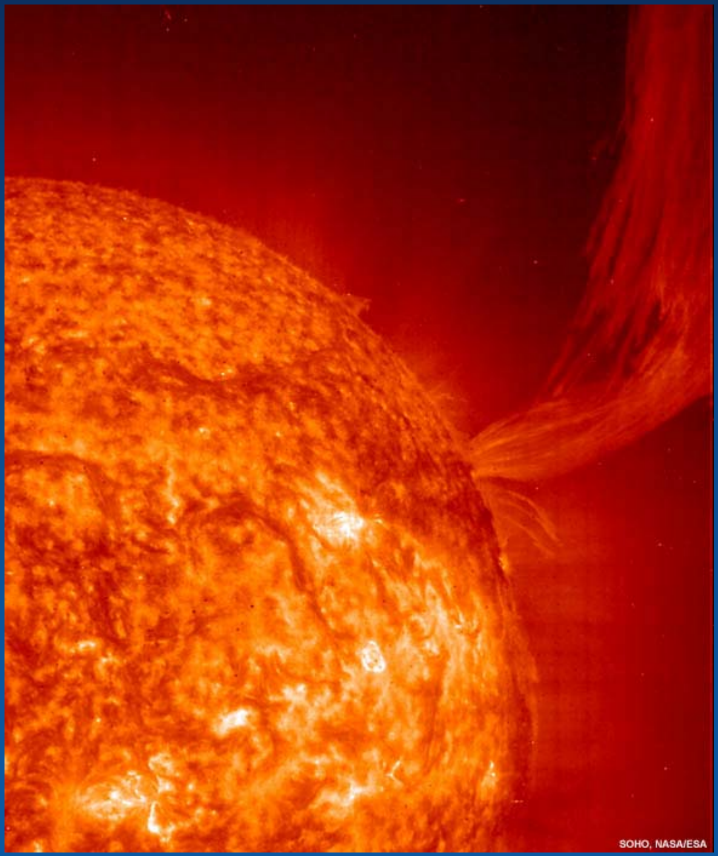
Sustainable Paths to Hydrogen



Direct Conversion Systems

Visible light has sufficient energy to split water (H_2O) into **Hydrogen and Oxygen**

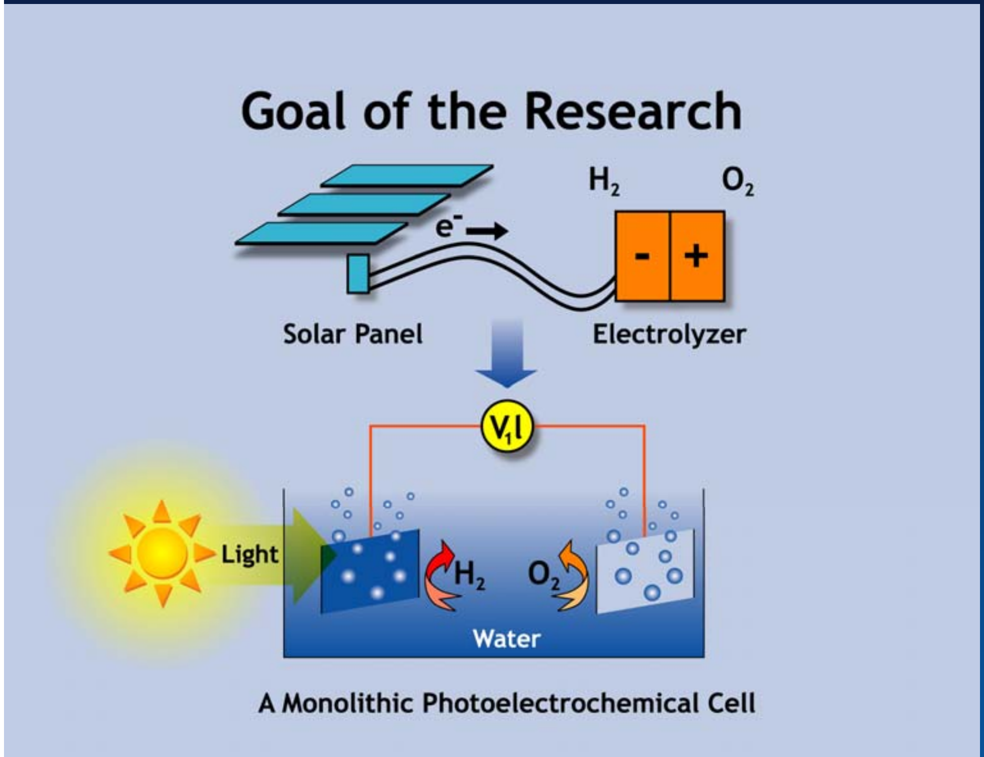
Combination of a Light Harvesting System and a Water Splitting System



- ✓ Semiconductor photoelectrolysis
- ✓ Photobiological Systems
- ✓ Homogeneous water splitting
- ✓ Heterogeneous water splitting
- ✓ Thermal cycles

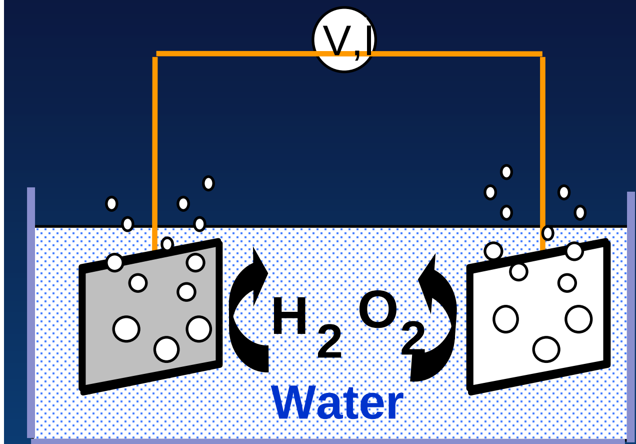
(Sunlight and Water to Hydrogen with No External Electron Flow)

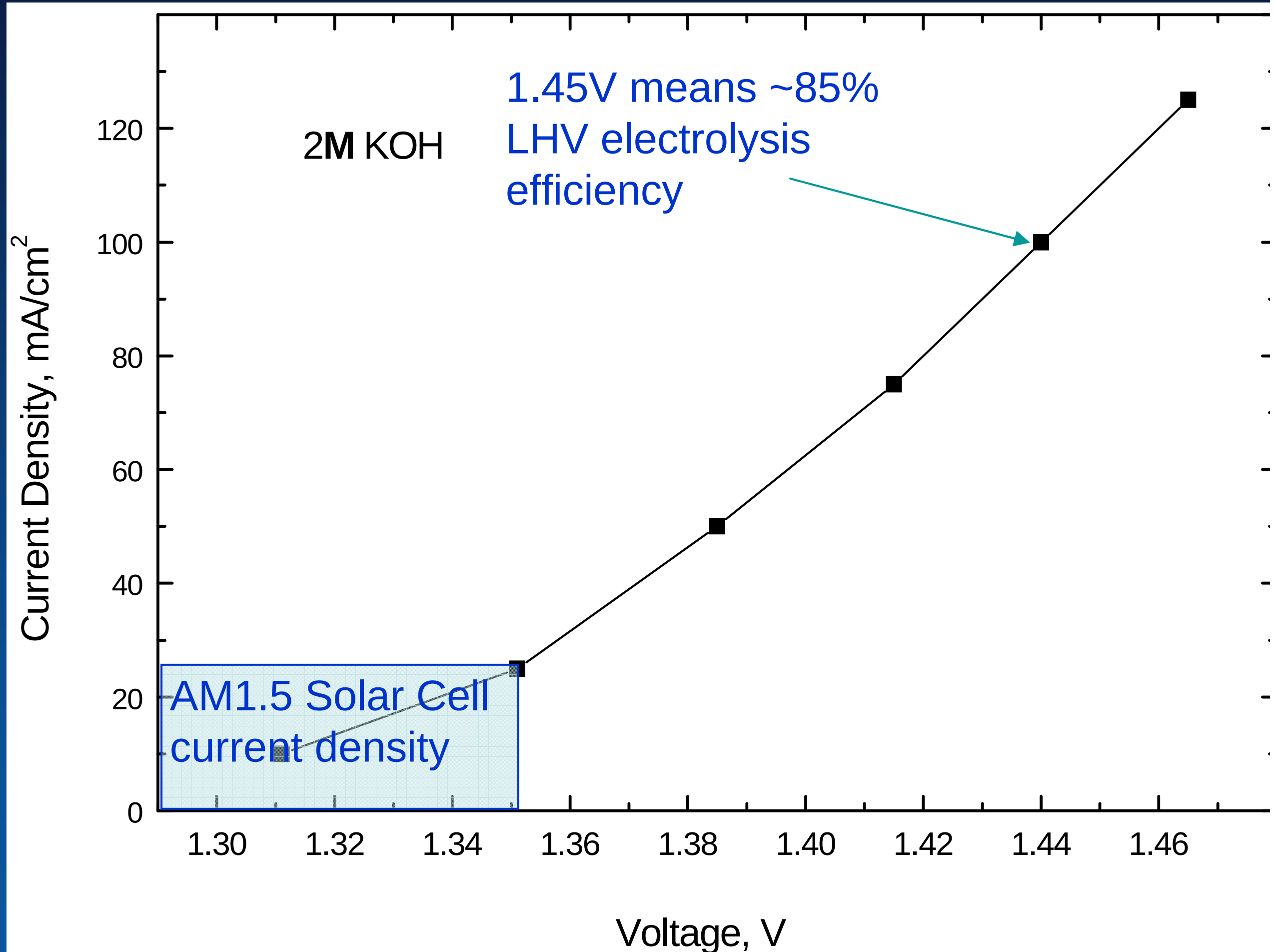
Photoelectrochemical-Based Direct Conversion Systems



- Combines a photovoltaic system (light harvesting) and an electrolyzer (water splitting) into a single monolithic device.
  - Electrolysis area approximates that of the solar cell - the current density is reduced.
  - Efficiency can be 30% higher than separated system.
- Balance of system costs reduced.
  - Capital cost of electrolyzer eliminated
- Semiconductor processing reduced.

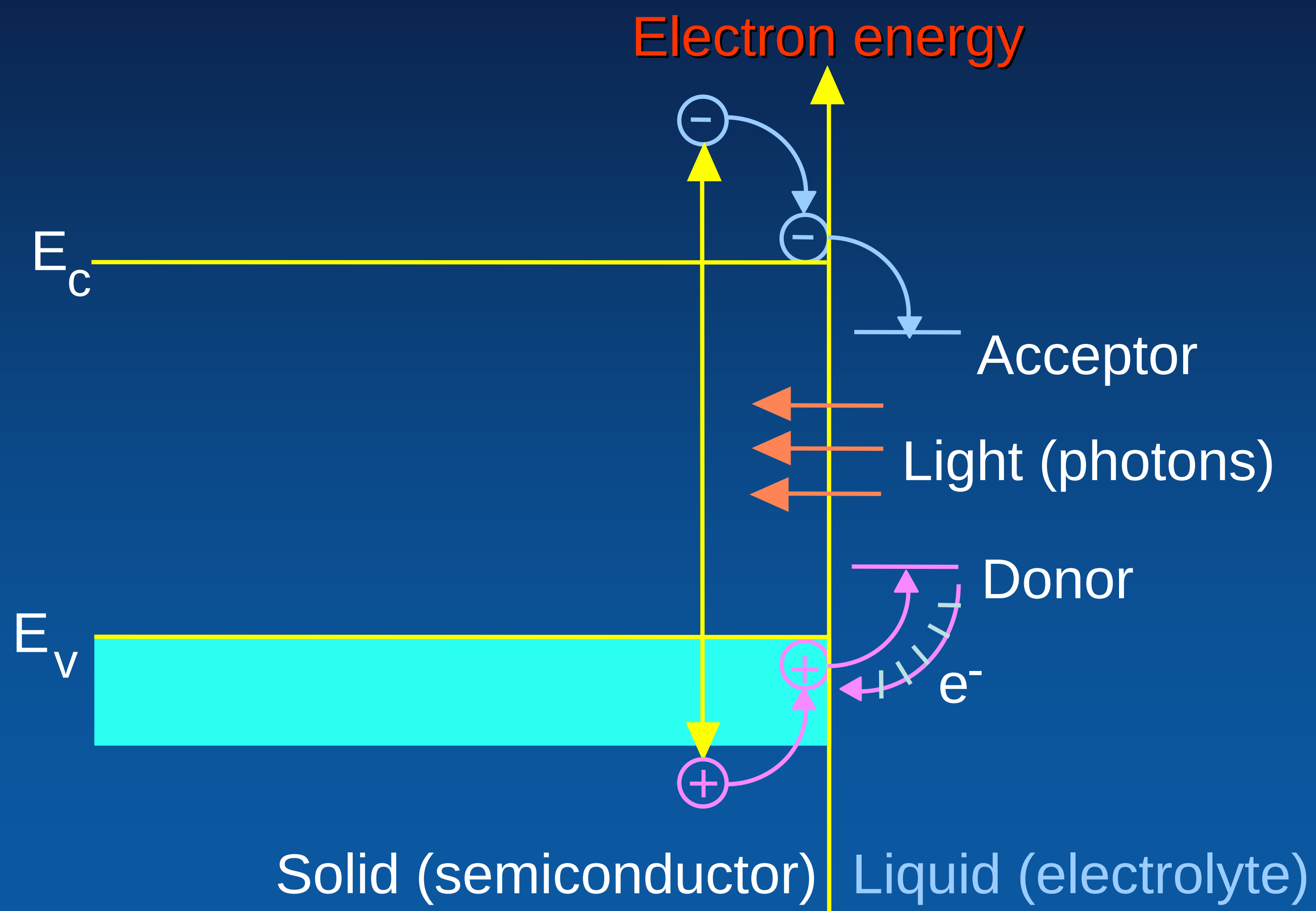
Current Density vs. Voltage for 2 Pt Electrodes of Equal Area.



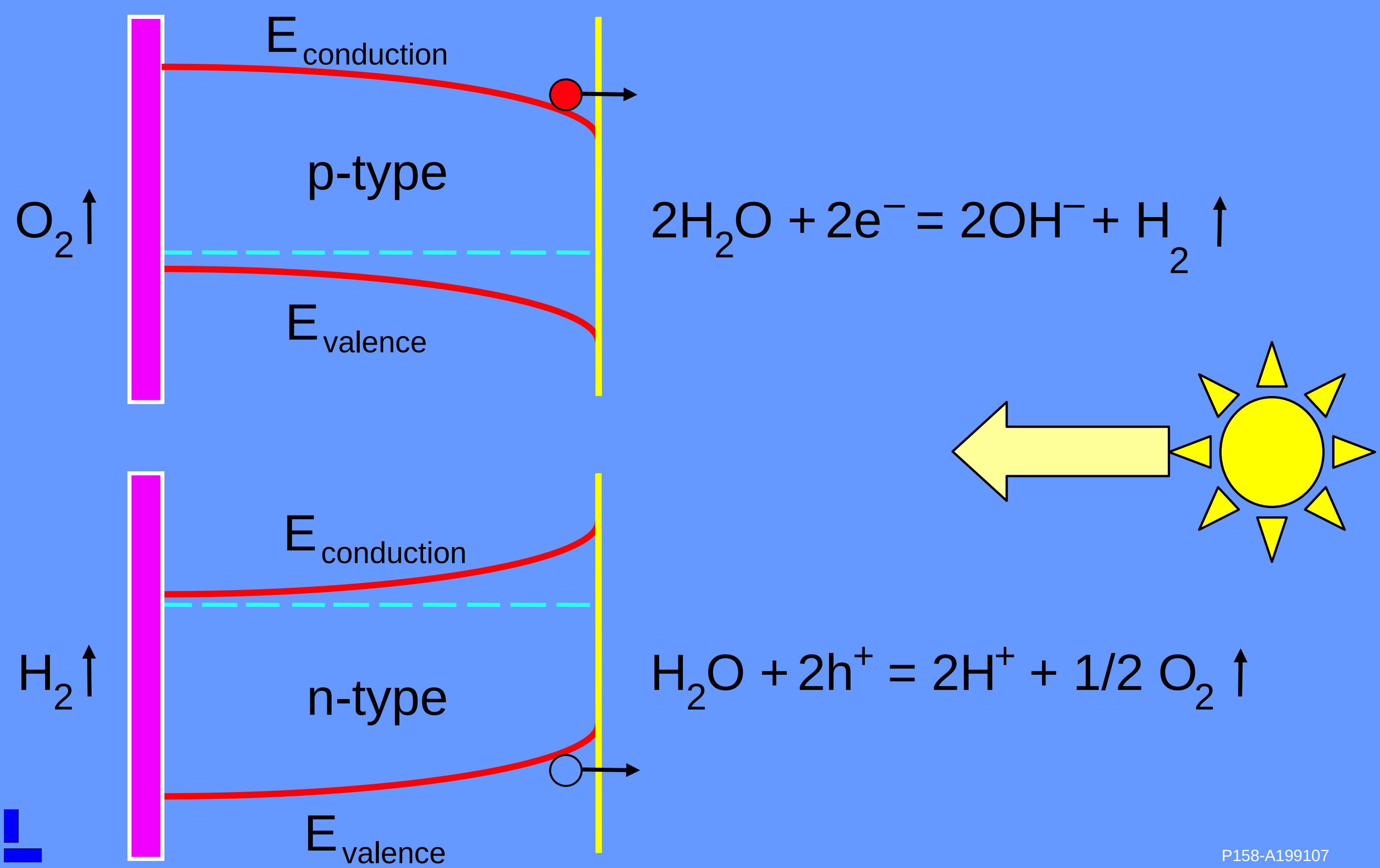


O. Khaselev, A. Bansal and J. A. Turner, *International Journal of Hydrogen Energy*, **26**, p 127-132 (2001).

Chemical Reactions at a Semiconductor Electrolyte Interphase



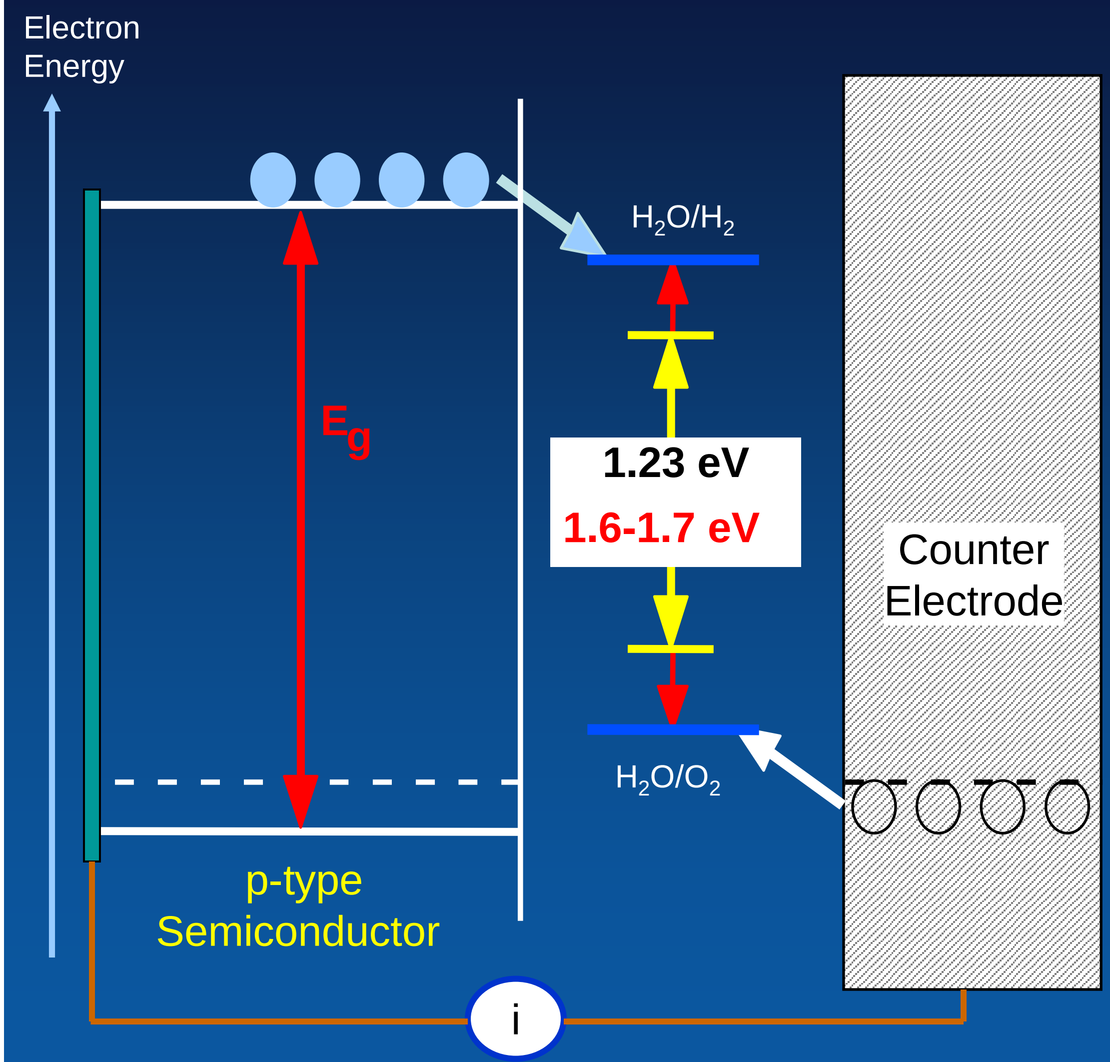
Band Edges of p- and n-Type Semiconductors Immersed in Aqueous Electrolytes to Form Liquid Junctions



P158-A199107

Technical Challenges *(the big three)*

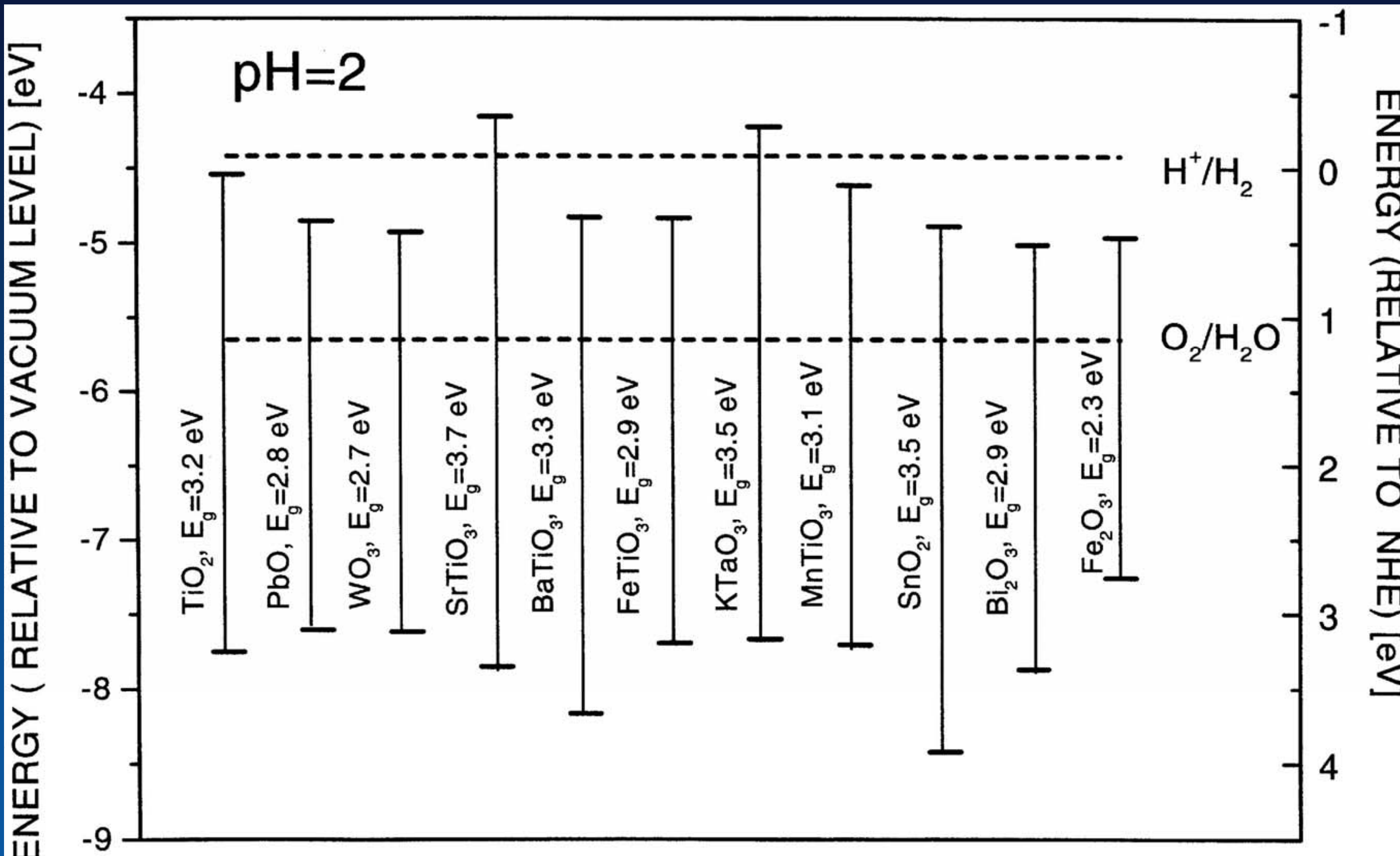
Material Characteristics for Photoelectrochemical Hydrogen Production



- **Efficiency –** the band gap (E_g) must be at least 1.6-1.7 eV, but not over 2.2 eV, high photon to electron conversion.
- **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

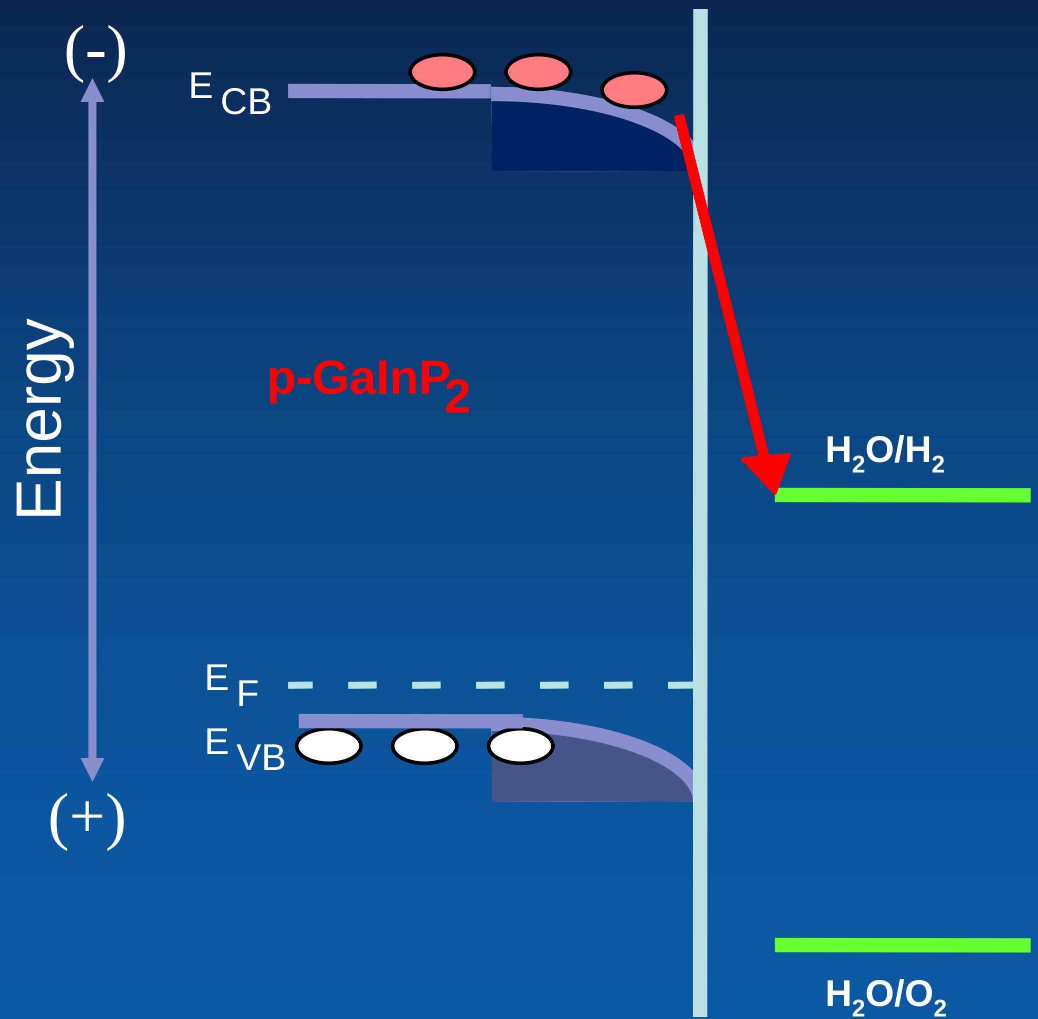
Bandedge Energetic Considerations



T. Bak, J. Nowotny, M. Rekas, C.C. Sorrell, International Journal of Hydrogen Energy **27** (2002) 991– 1022

Gallium Indium Phosphide/Electrolyte System

Used to gain a fundamental understanding of semiconductor/electrolyte junctions

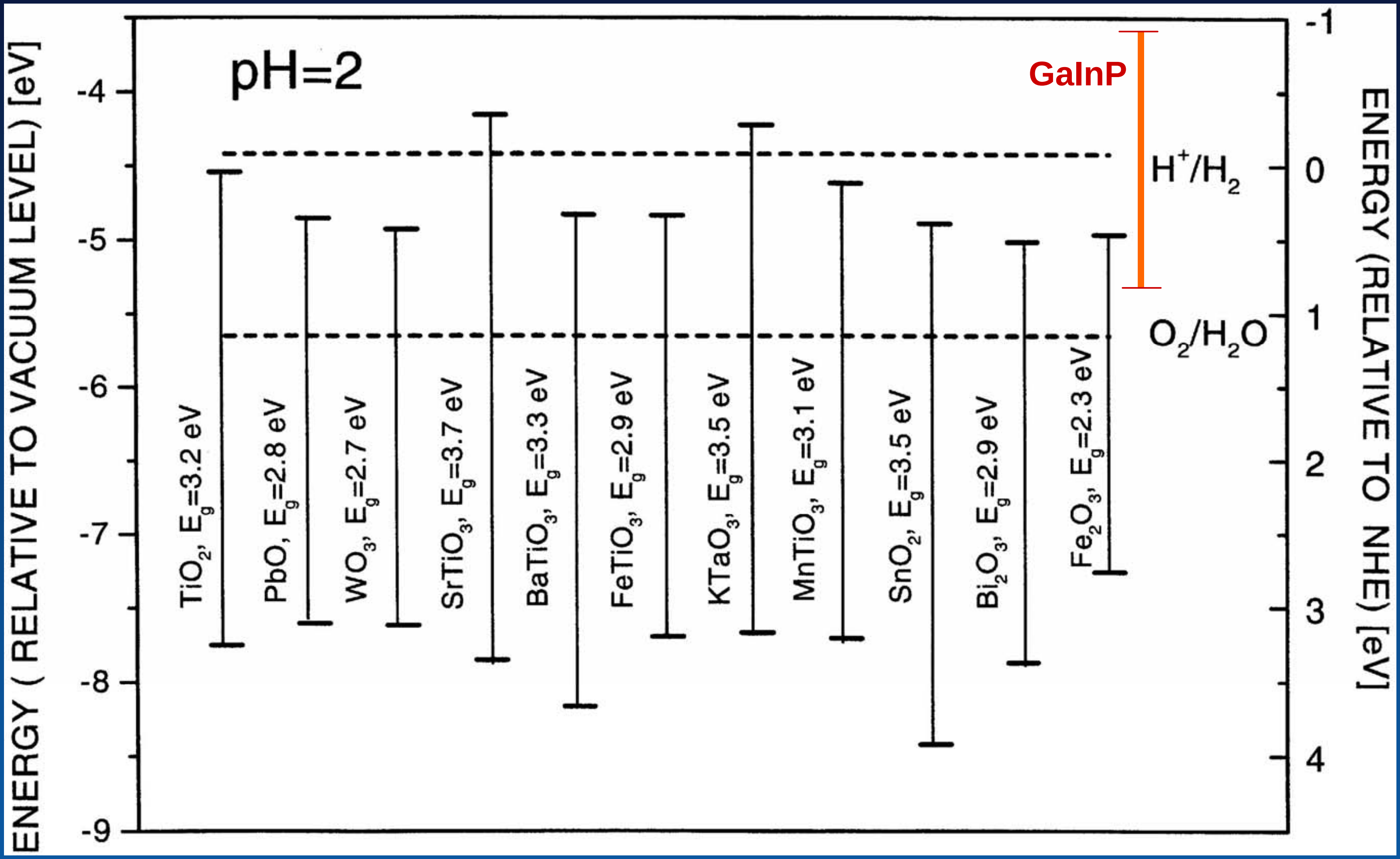


Eg = 1.83 eV
OK

Band edges are too negative

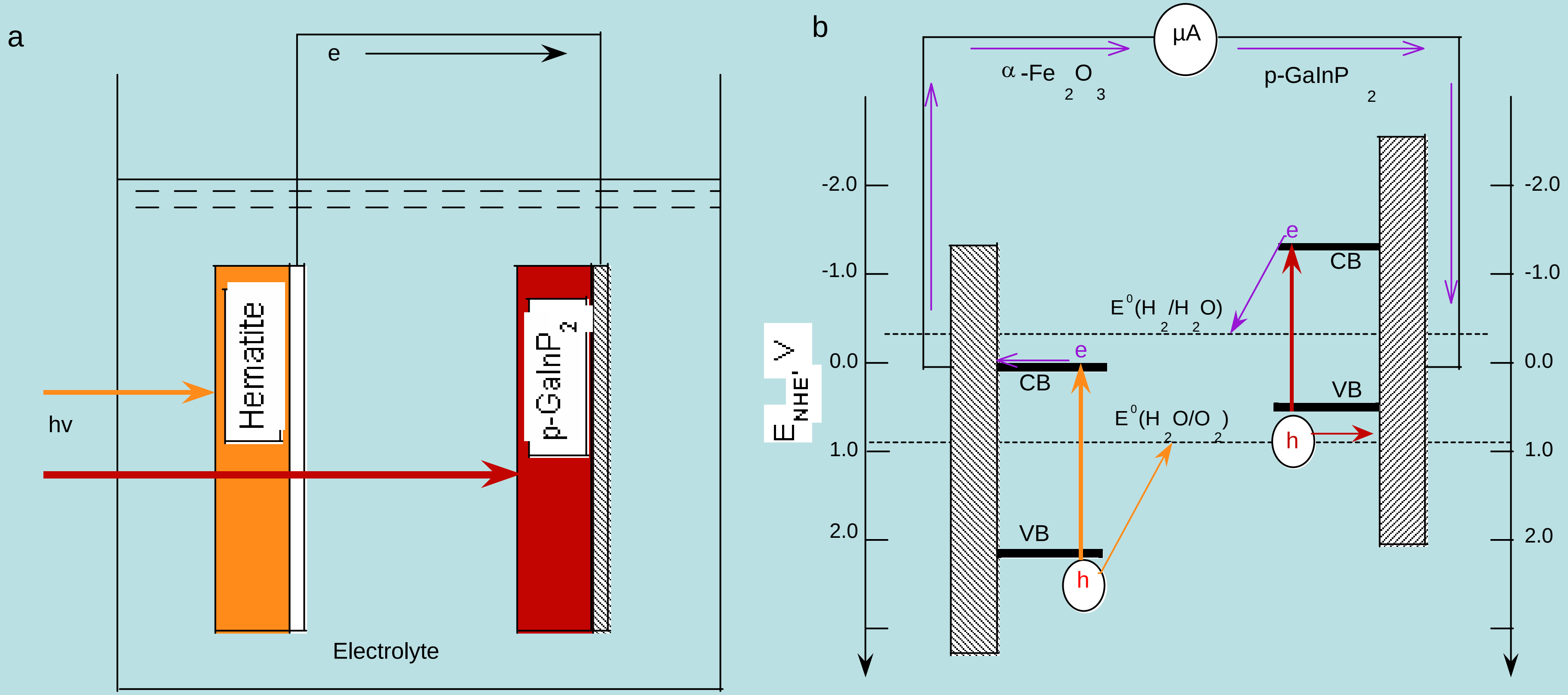
Band edges are pH sensitive

Bandedge Energetic Considerations



T. Bak, J. Nowotny, M. Rekas, C.C. Sorrell, International Journal of Hydrogen Energy **27** (2002) 991– 1022

Dual Photoelectrode Approach for Bandedge Mismatch and Stability Issues



Lower cost Fe_2O_3 electrode is a possibility, but while the system splits water, the efficiency is very low.

Metal Oxides – A materials assessment

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

- Transitions which impart color to the oxides typically involve d and f levels and are generally forbidden transitions = low absorption coefficients.
  - The low absorption coefficients result in the incident light penetrating deep into the material = 100's um of material
- Carrier mobilities in oxides are very low
  - Recombination of photogenerated carriers occurs before they can reach the semiconductor/electrolyte interface.
- Even good single crystals of metal oxides have very low energy conversion efficiencies due to inherently short diffusion lengths.

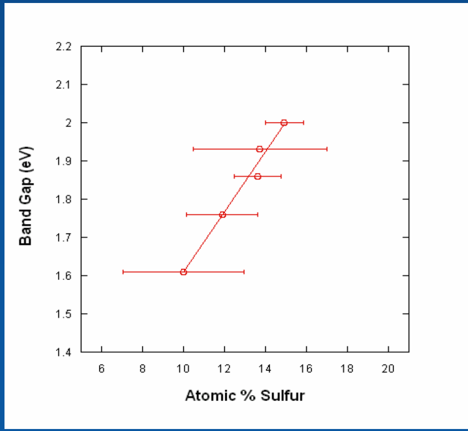
However a success in this area, e.g. an oxide with good to excellent conversion properties could revolutionize the PV industry as well as make PEC near-term.

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

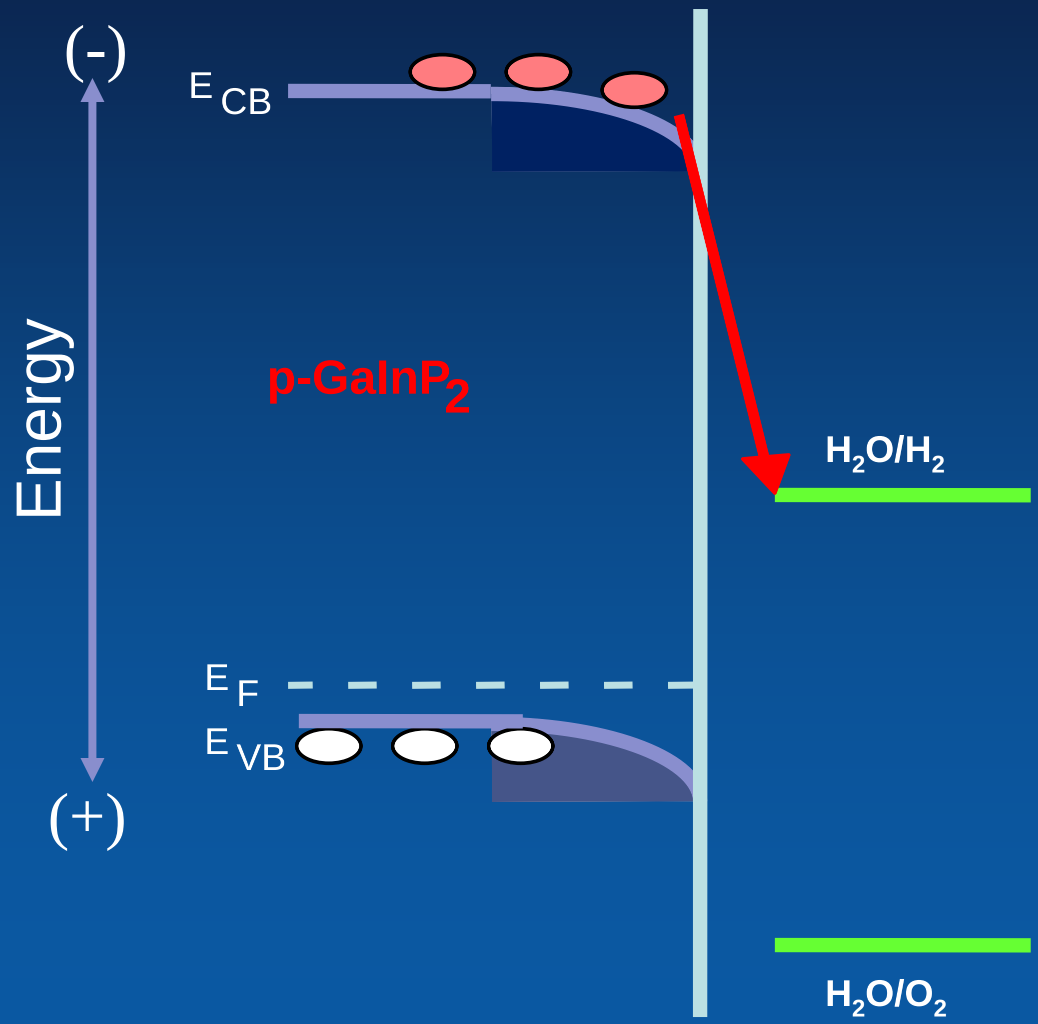
Approach: Materials Summary

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 *Green*:

- ✓ *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

Gallium Indium Phosphide/Electrolyte System

Used to gain a fundamental understanding of semiconductor/electrolyte junctions

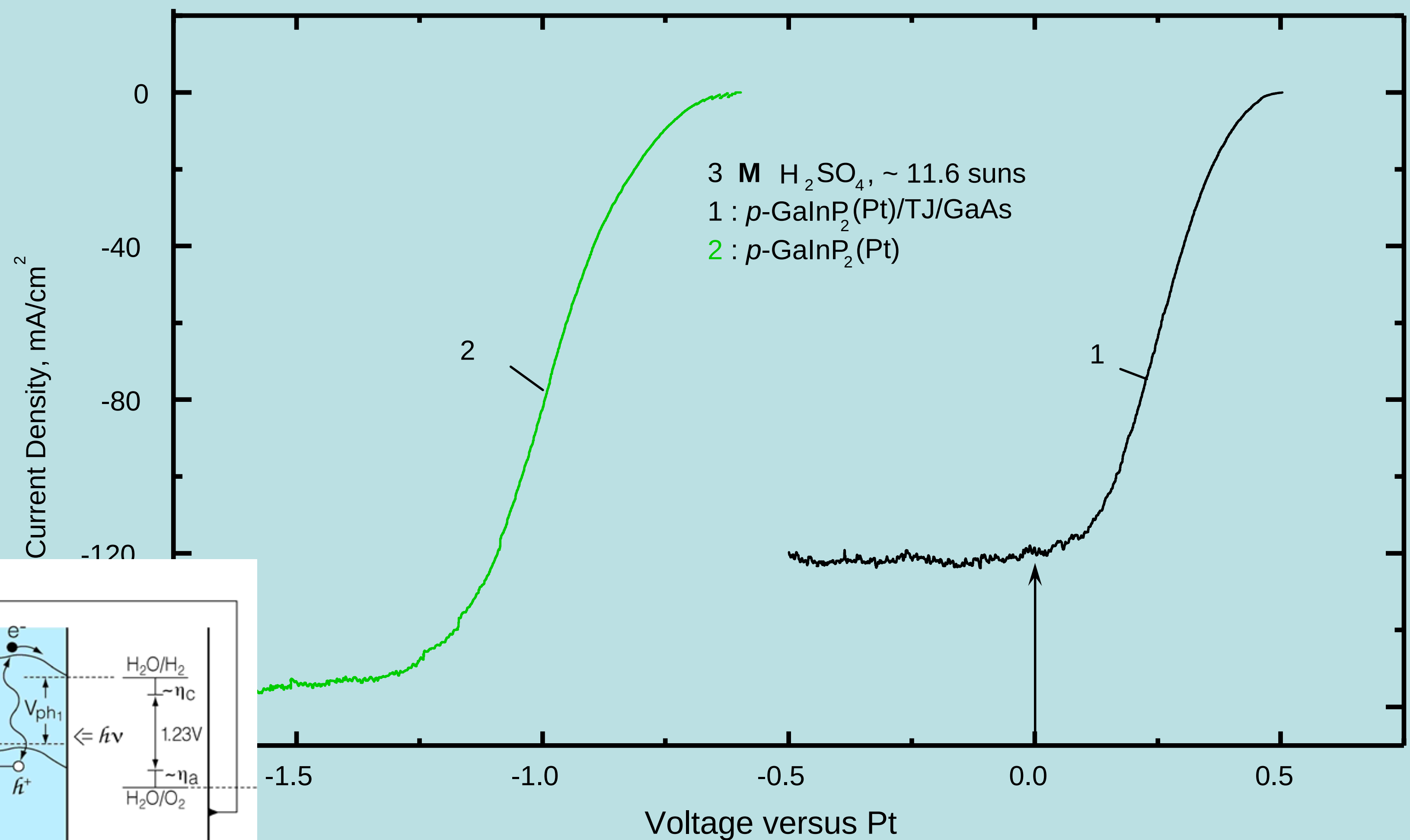


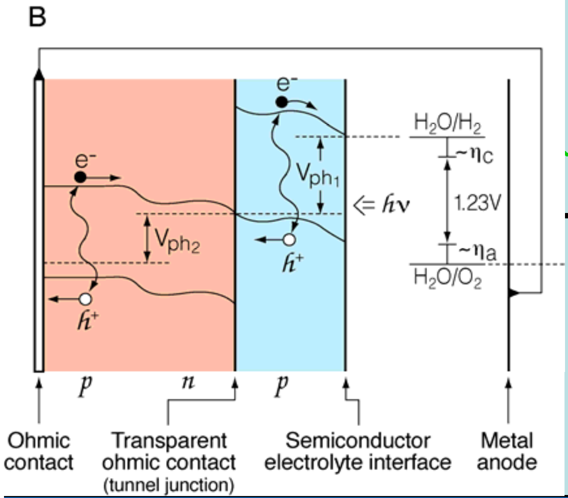
Eg = 1.83 eV
OK

Band edges are too negative

Band edges are pH sensitive

Review: Comparison of *p*-GaInP$_2$ and PEC/PV device

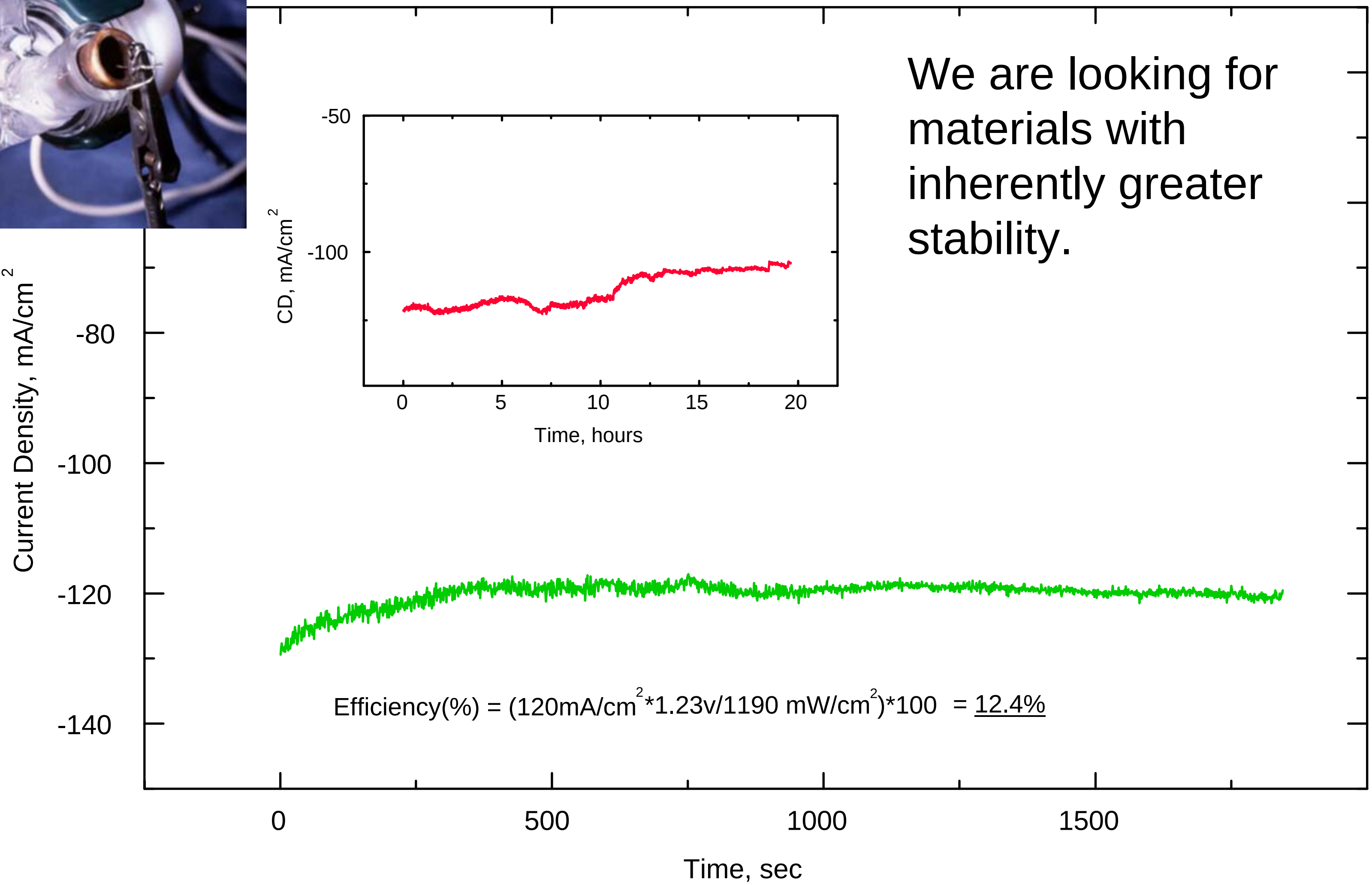




The GaAs integrated PV cell compensates for the energetic mismatch – but lifetime...

Photocurrent time profile for PEC/PV Water-Splitting device, showing current decay due to corrosion.

O. Khaselev and J. A. Turner, Science, **280**, pg 425 (1998).



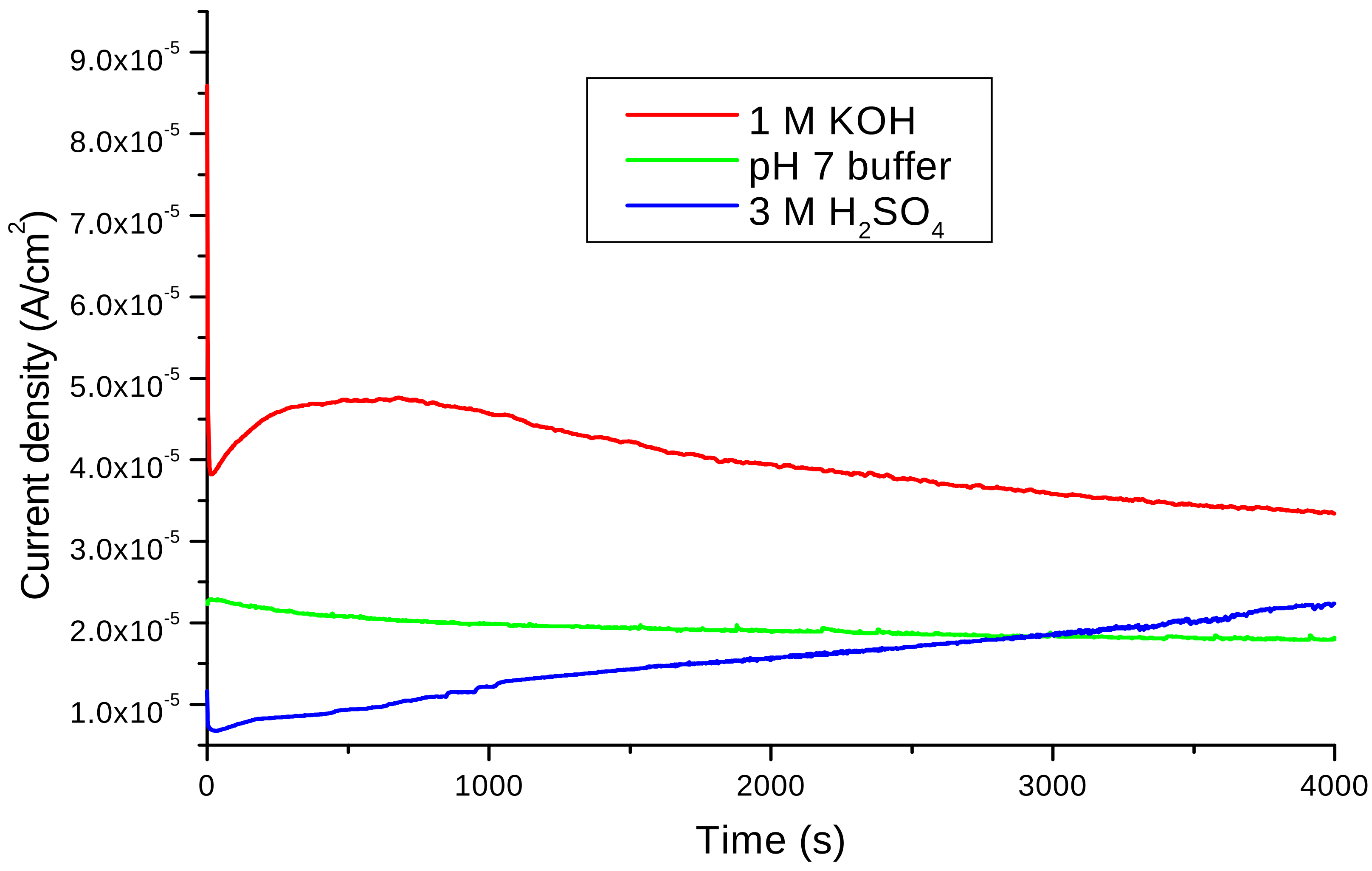
We are looking for materials with inherently greater stability.

Elemental Abundances in Earth's Crust

Element	Concentration (mg/kg)	Element	Concentration (mg/kg)
Gallium	19	P	1050
Lead	14	Silicon	2.8×10^5
Boron	10	Indium	0.25
Lithium	20	Silver	0.075
Tungsten	1.25	Tin	2.3
Cobalt	25	Uranium	2.7

Gallium is found in bauxite (aluminum ore). There are 2 million kg of Ga in Arkansas bauxite deposits alone. Also found in coal ash (up to 1.5%).

Hydrogen Evolution Current-Time Profile for *p*-GaN

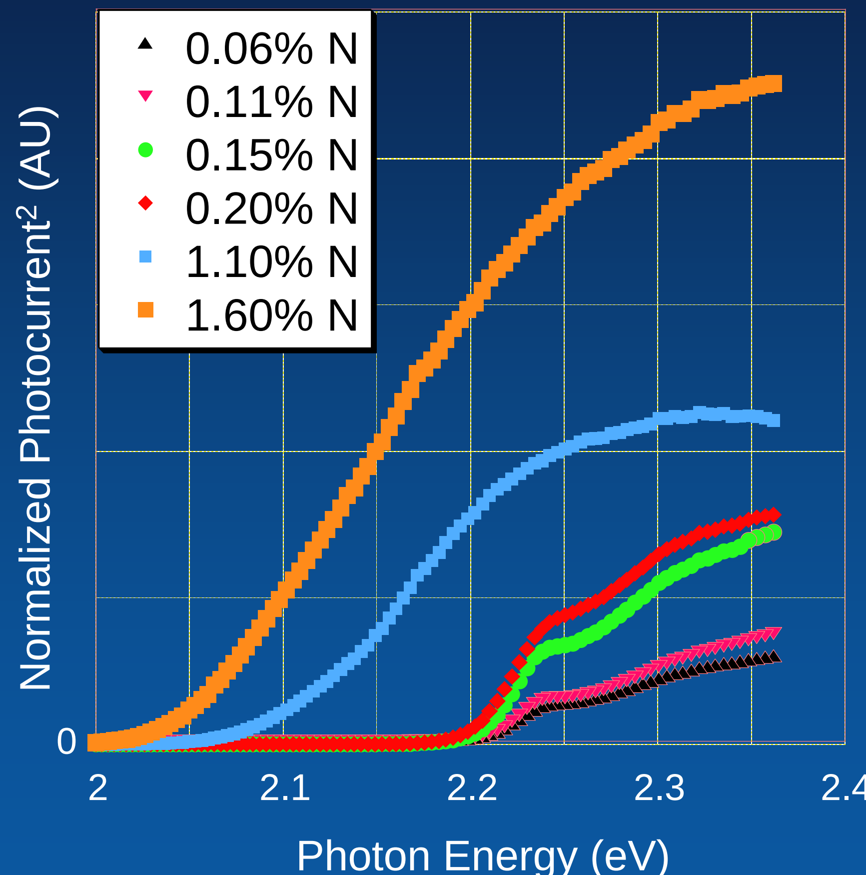


S. Kocha, M. Peterson, D. J. Arent, J. M. Redwing, M. A. Tischler and J. A. Turner, "Electrochemical Investigation of the Gallium Nitride-Aqueous Electrolyte Interface", *Journal of The Electrochemical Society*, **1995**,142, pg. L238-L240.

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



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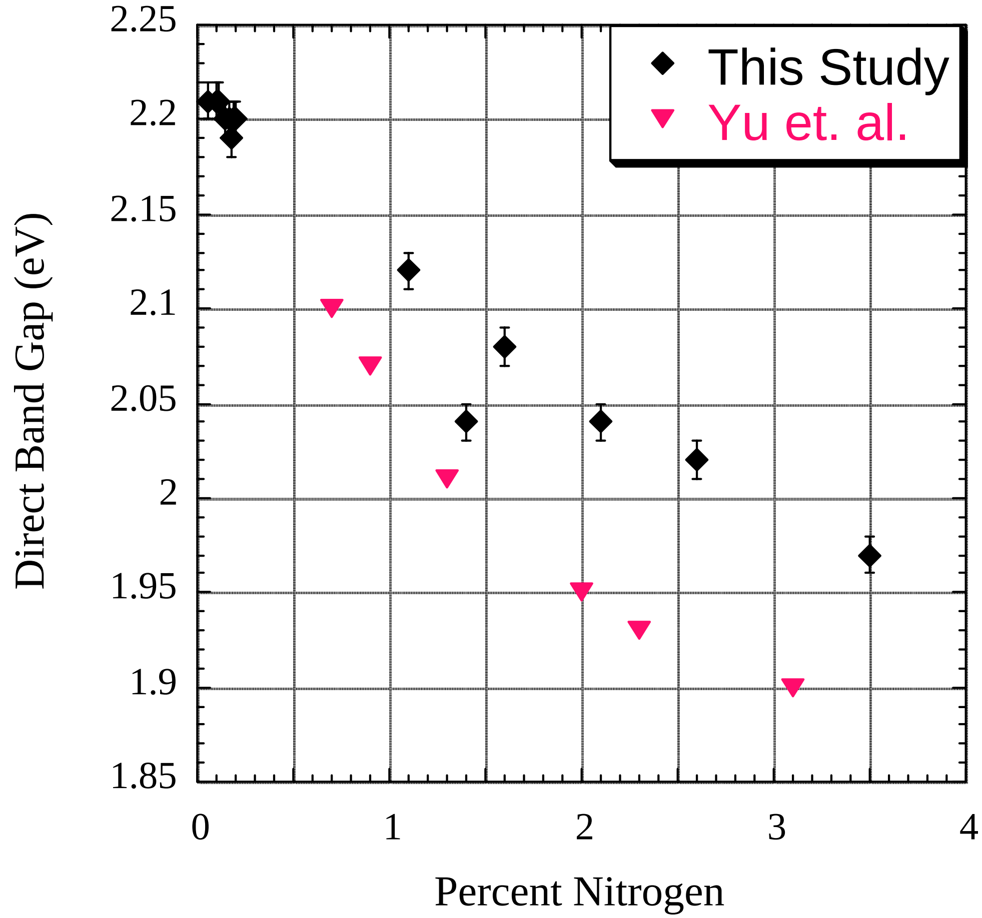
Goal: Stable III-V nitride material

$GaP_{1-x}N_x$ Bandgap as a Function of Nitrogen Concentration

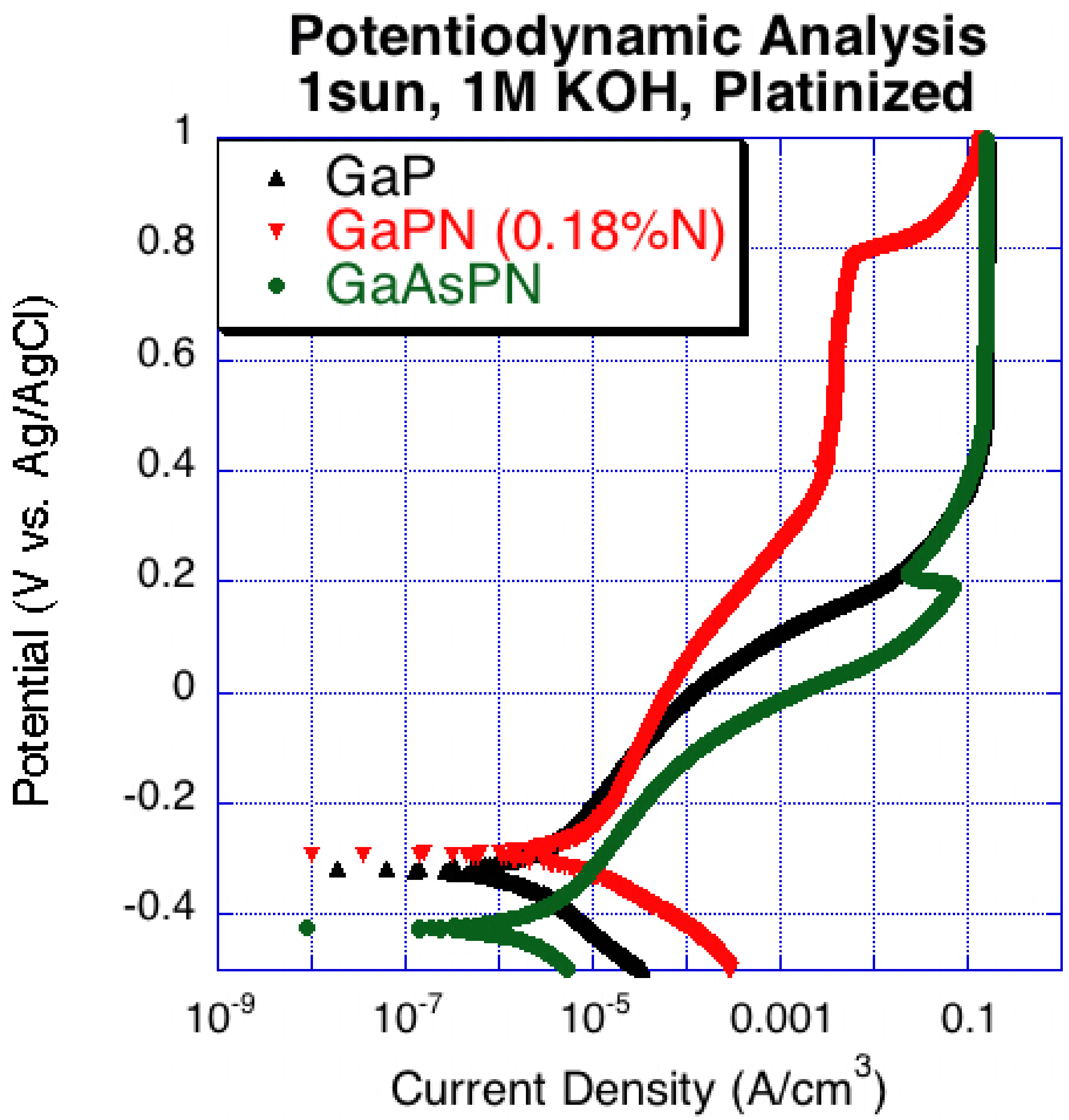
- Control band gap energy by varying nitrogen composition,
- Direct band gap for all nitrogen concentrations, even at $GaP_{.9994}N_{.0006}$
- The crossover from indirect to direct occurs significantly below the theoretically predicted 0.26%

(F. Benkabou, J. P. Becker, M. Certier, H. Aourag, Calculation of Electronic and Optical Properties of Zinc Blende GaP1-xNx. Superlattices and Microstructures, 1998. 23(2): p. 453-465.)



K.M. Yu, W. Shan, J. Wu, Nature of the fundamental band gap in GaN_xP_{1-x} alloys. Applied Physics Letters, 2000. 76(22): p. 3251-3253

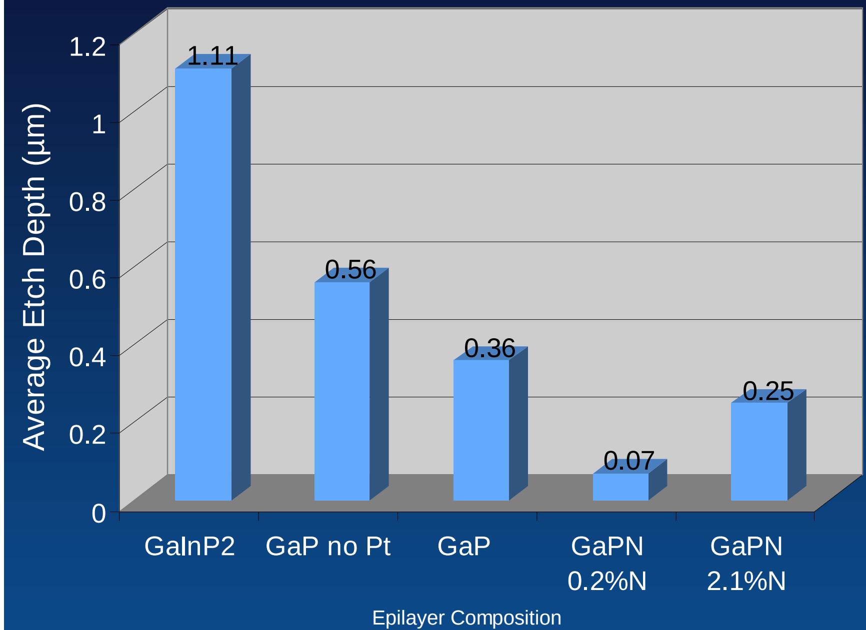
Goal: Stable III-V nitride material

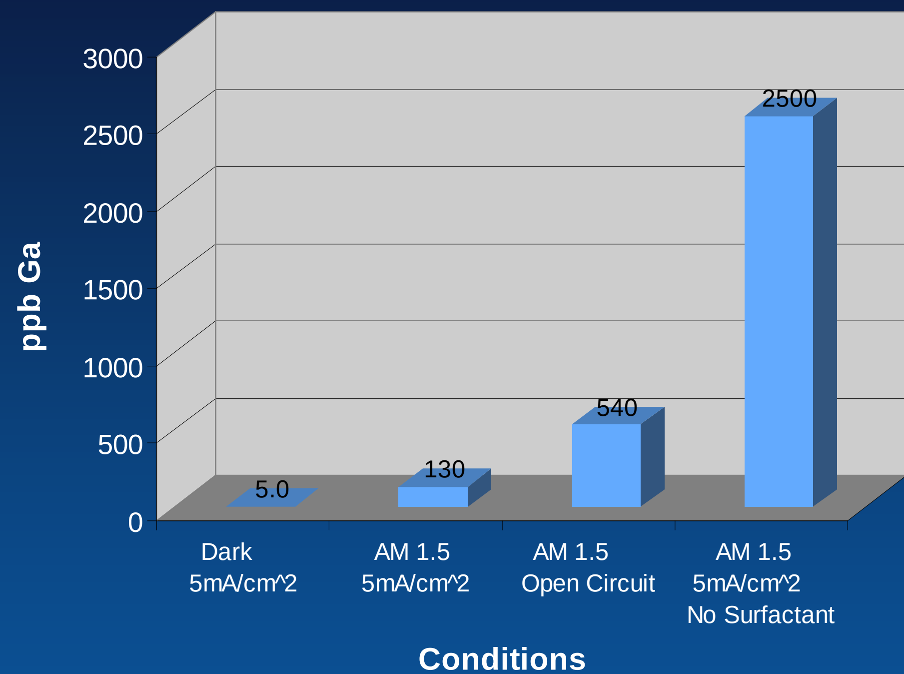


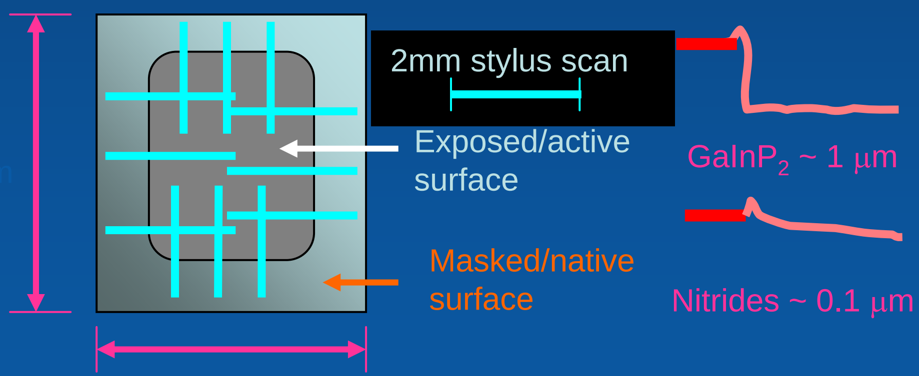
Corrosion experiments on GaP substrate clearly show the enhanced corrosion resistance from nitrogen addition.

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

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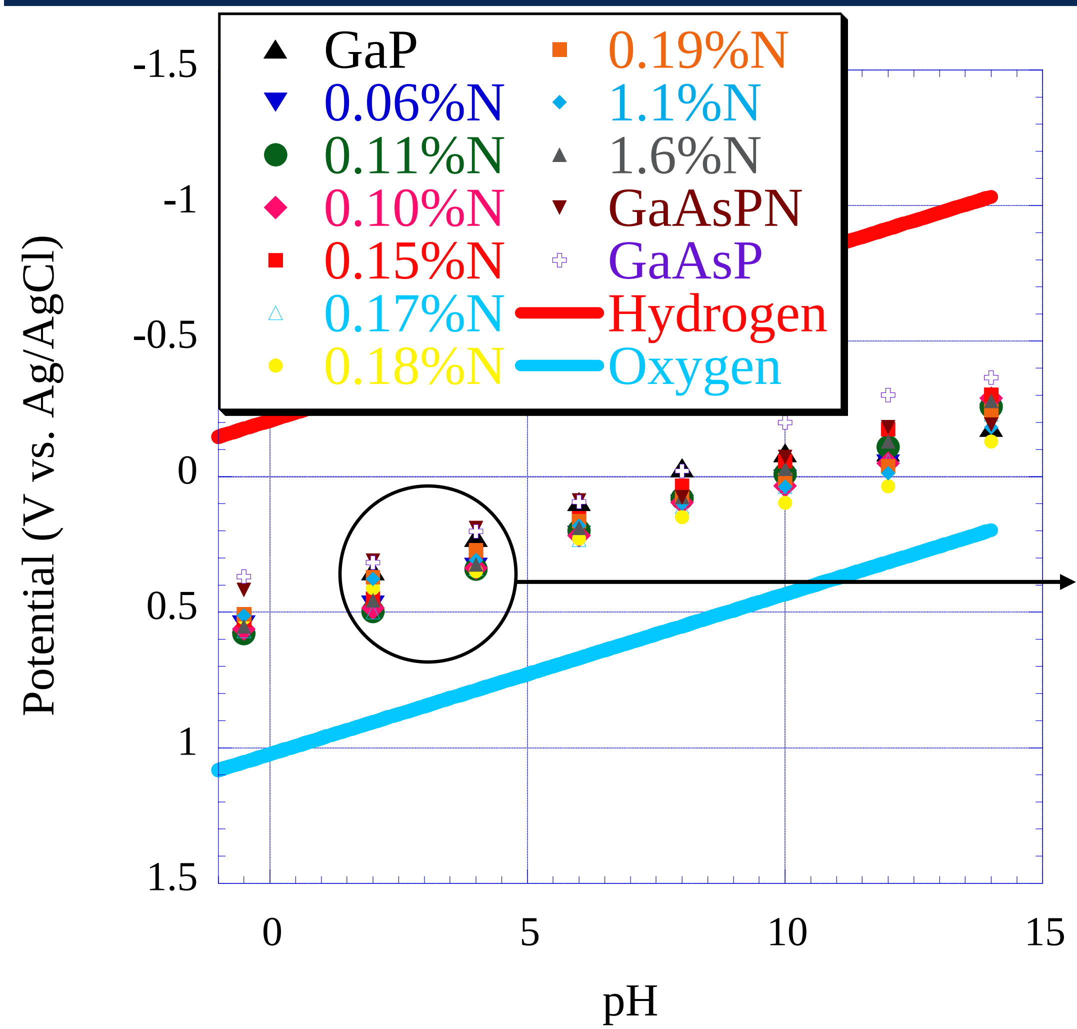
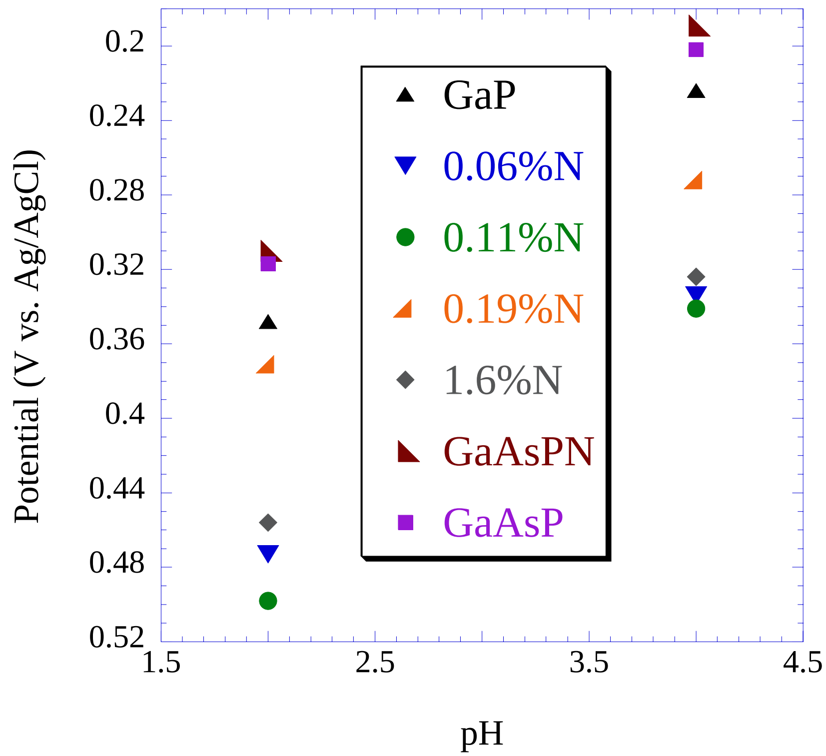
Goal: Stable III-V nitride material

Band Edge Energetics

The band edges of these materials are too negative for spontaneous water-splitting.

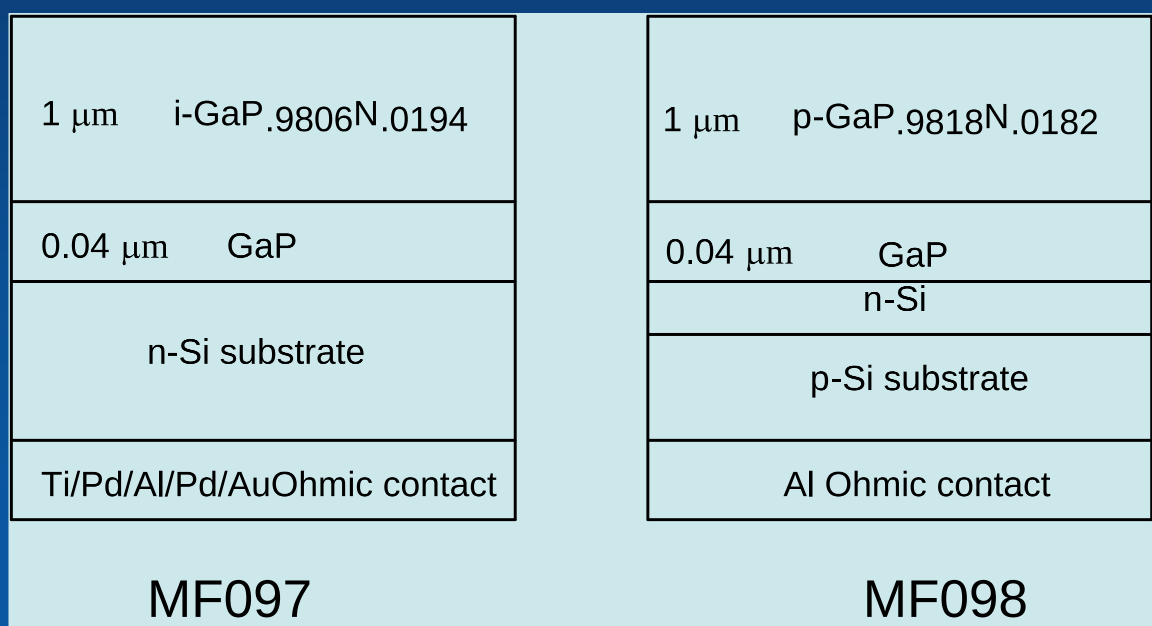




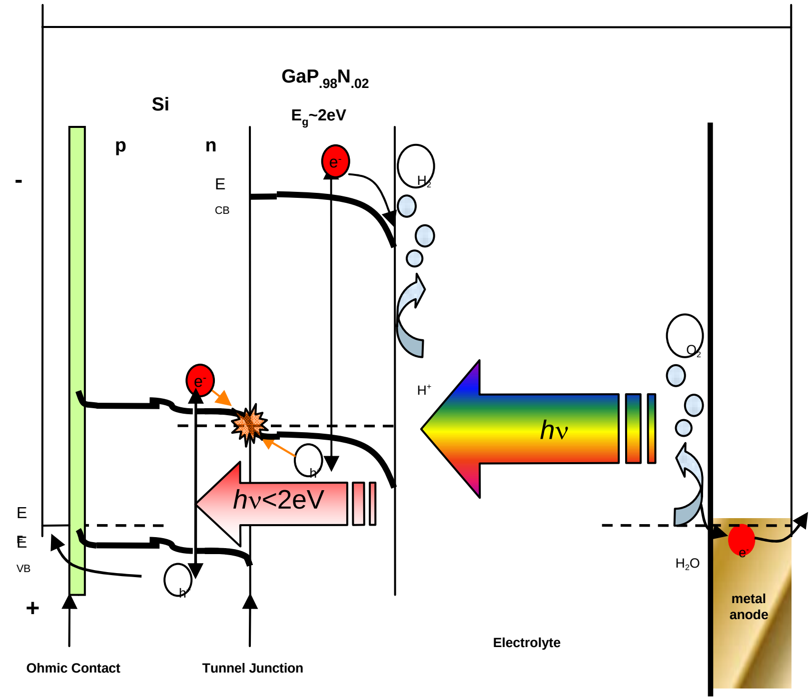
Approach: Two configurations

One for material study and one for possible high-efficiency tandem cell.

- GaPN/tj/ p-GaP or n-silicon substrate
  - Undoped
  - No low energy transition expected
- GaPN/tj/ p/n silicon substrate (tandem)
  - Undoped
  - Low energy transition expected

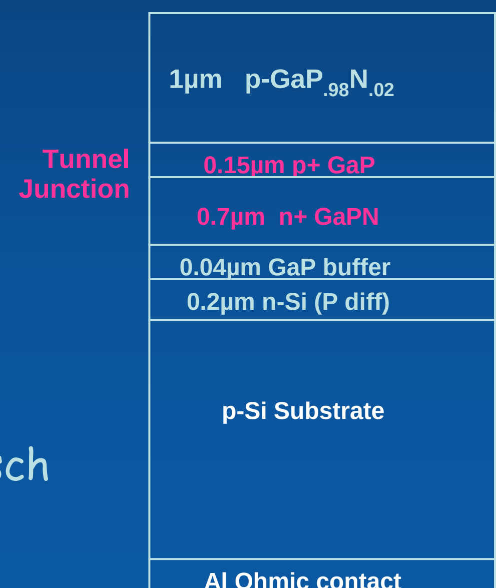


Goal: Stable III-V nitride material



GaPN:Si Tandem Cell

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



Direct Eg (eV)
Nitrogen%

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%

20mm

25mm

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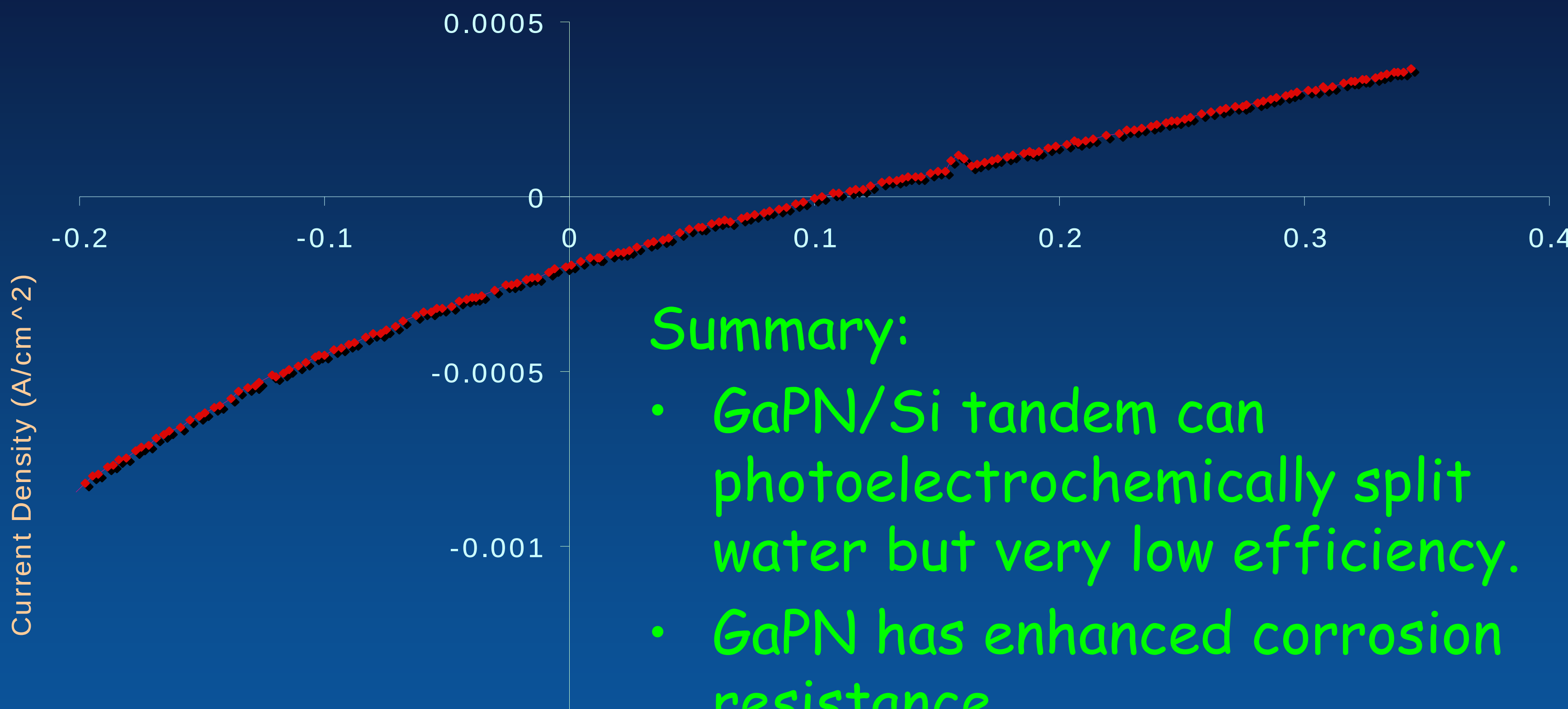
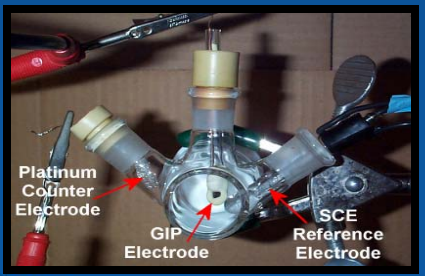
Light-Driven Water Splitting



Summary:

- GaPN/Si tandem can photoelectrochemically split water but very low efficiency.
- GaPN has enhanced corrosion resistance



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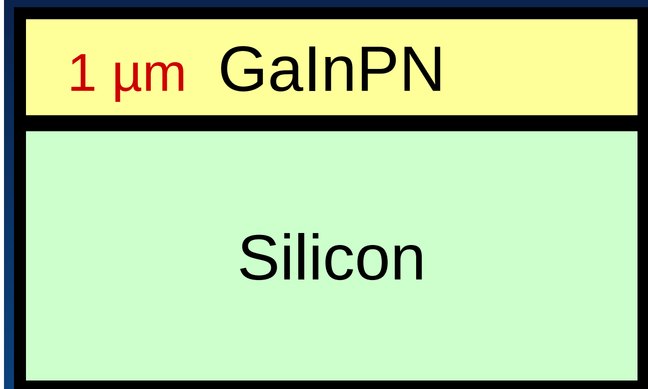
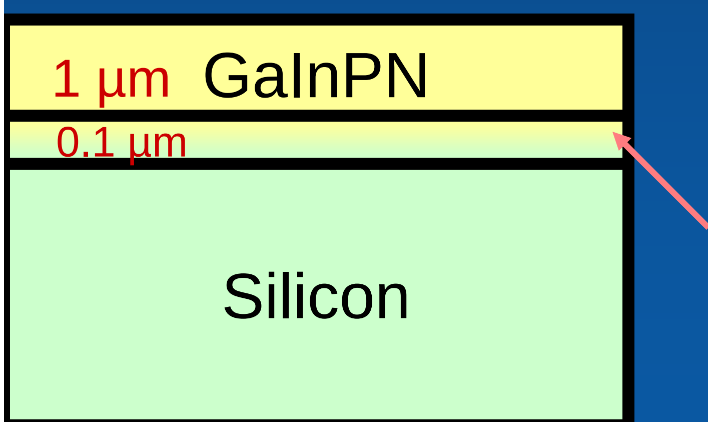
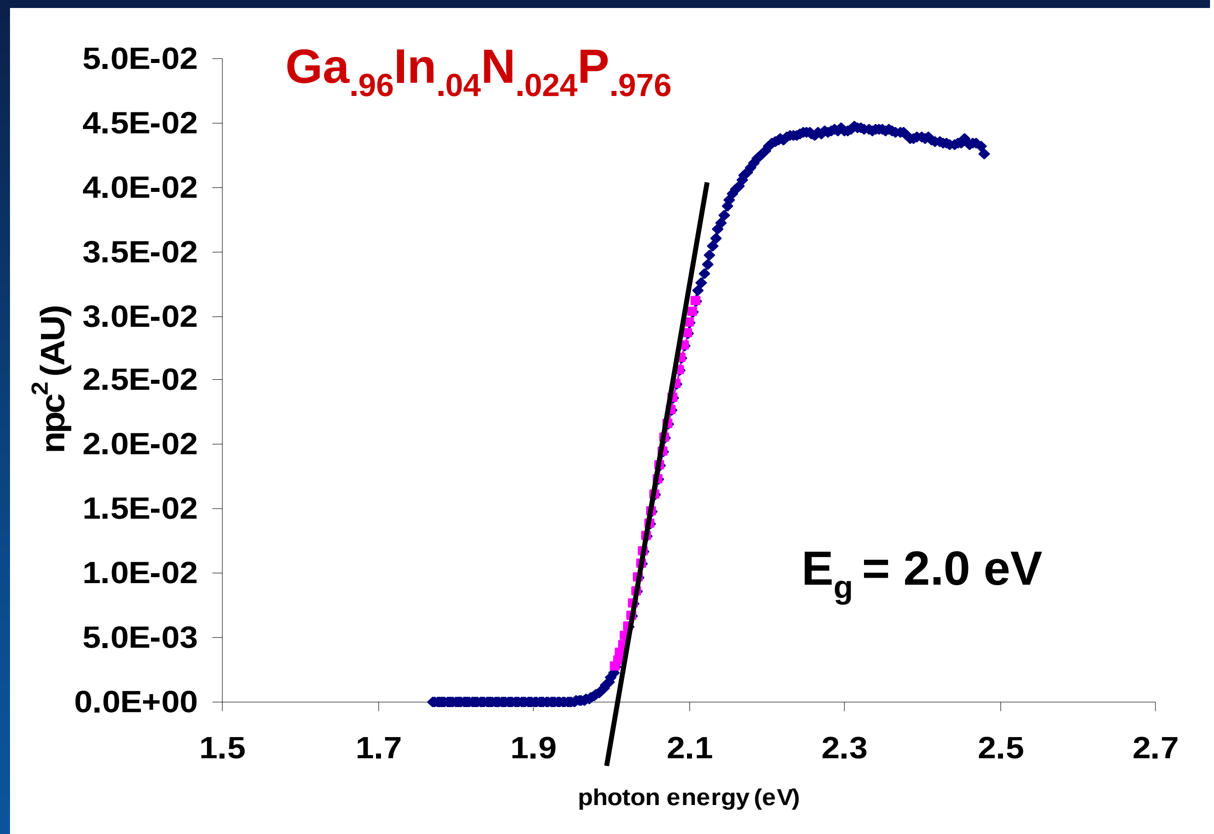
Goal: Stable III-V nitride material

GaInPN:Si – Two Tandem Cell Configurations







Zn-doped GaInPN

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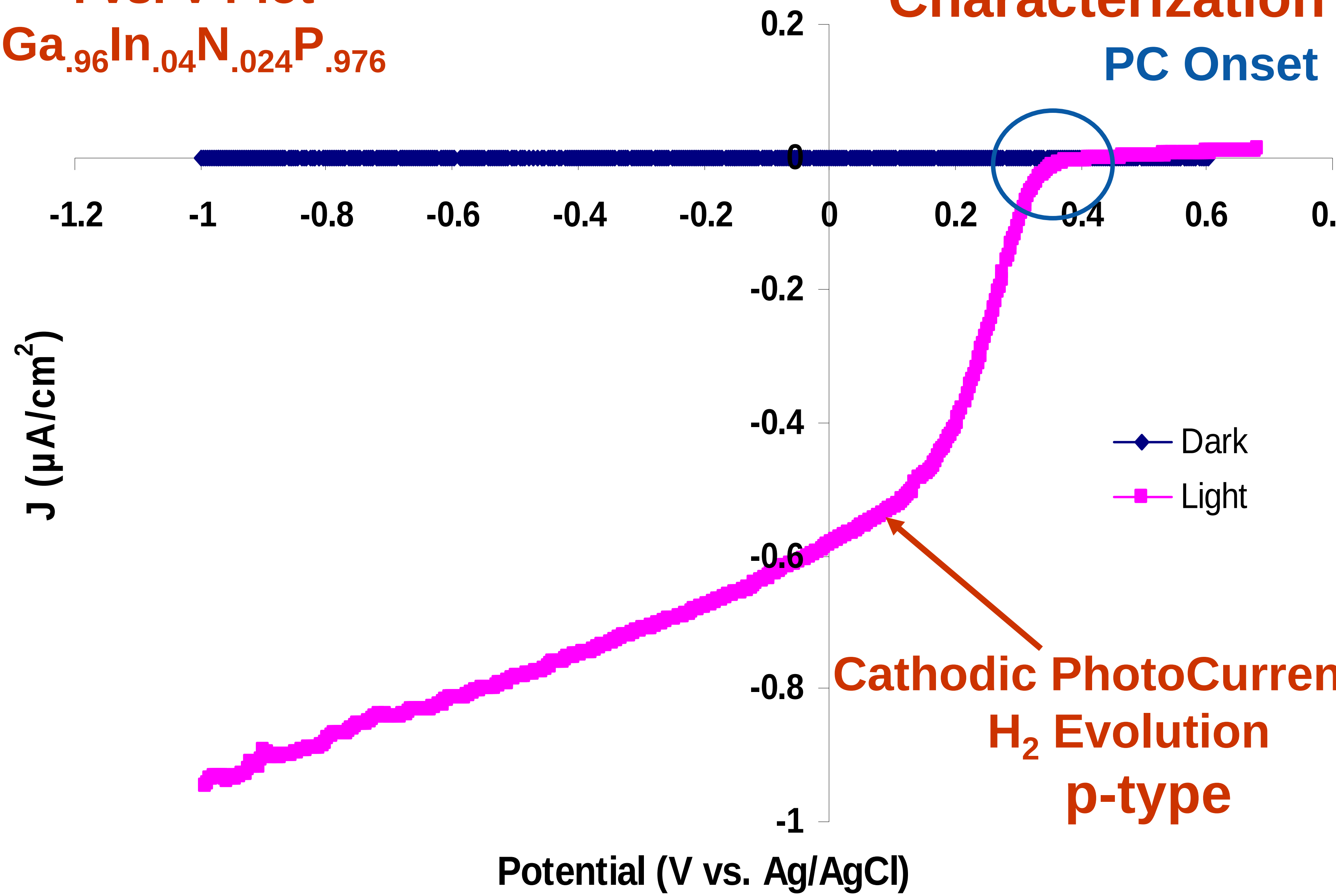
I vs. V Plot

$Ga_{.96}In_{.04}N_{.024}P_{.976}$

Characterization

PC Onset



Cathodic PhotoCurrent

H_2 Evolution

p-type

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Stability by Profilometry

$Ga_{.96}In_{.04}N_{.024}P_{.976}$:

Etched: 0.13µm/24hrs

$Ga_{.95}In_{.05}N_{.025}P_{.975}$:

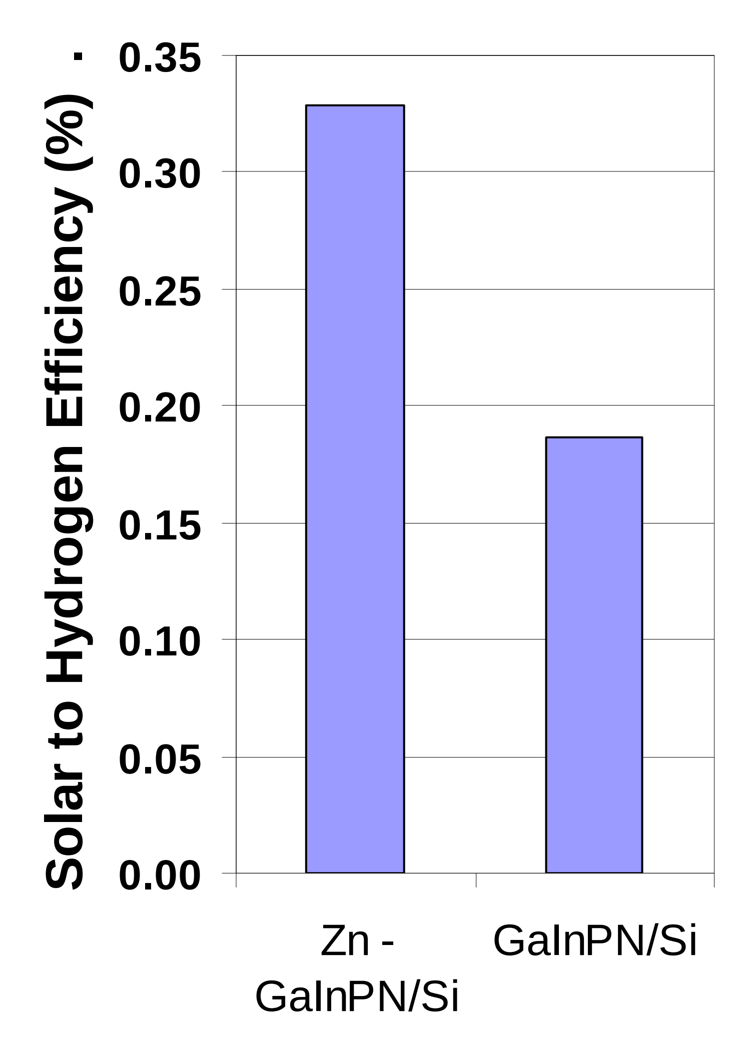
Etched: 0.14µm/24hrs

$GaInP_2$: 1-2µm/24hrs

Jeff Head, Paul Vallett

Water Splitting

- Photon to chemical energy conversion efficiency
  - GaInPN: ~30%
  - $GaInP_2$: ~90%
- Zn-doped layer improves efficiency
- Nitrogen decreases electronic properties of material



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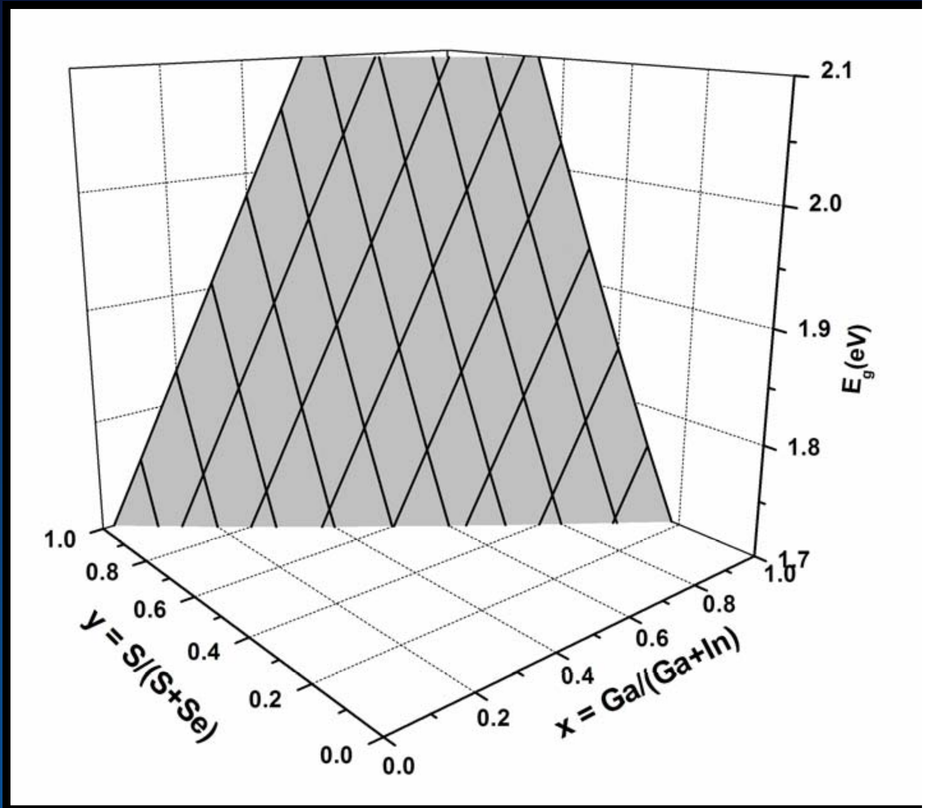
Electrodeposited CIGSS

- 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

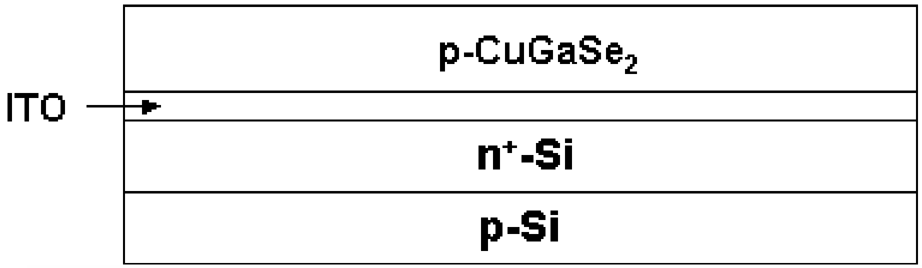
Dr. Jennifer E. Leisch

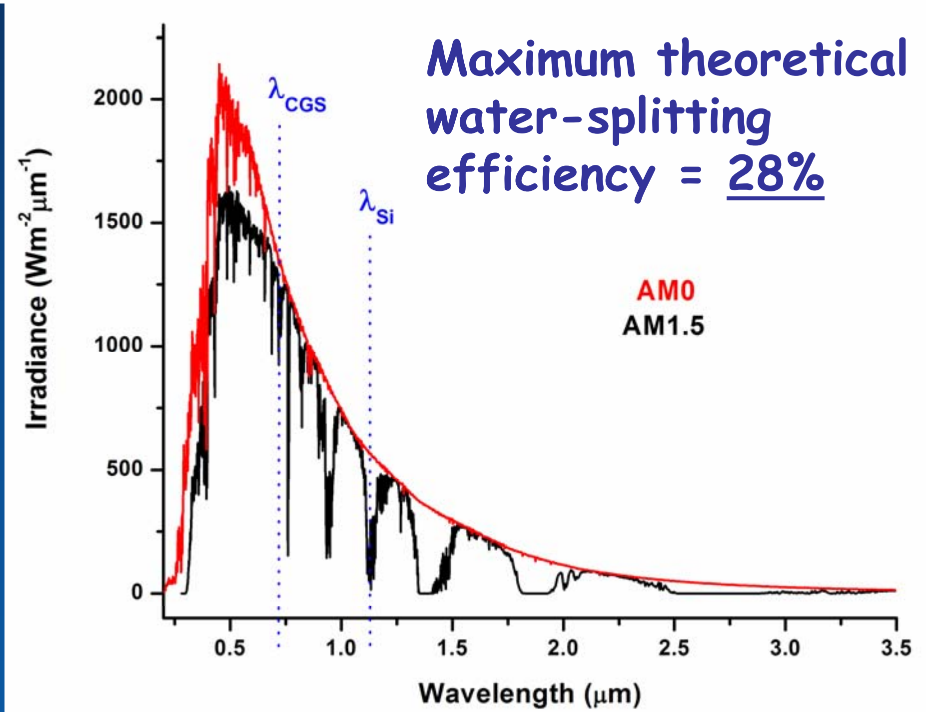
Goal: Evaluation of high efficiency thin-film material and thin-film based tandem cell

Goal: Thin-film based PEC tandem cell

Tandem Cell Configuration

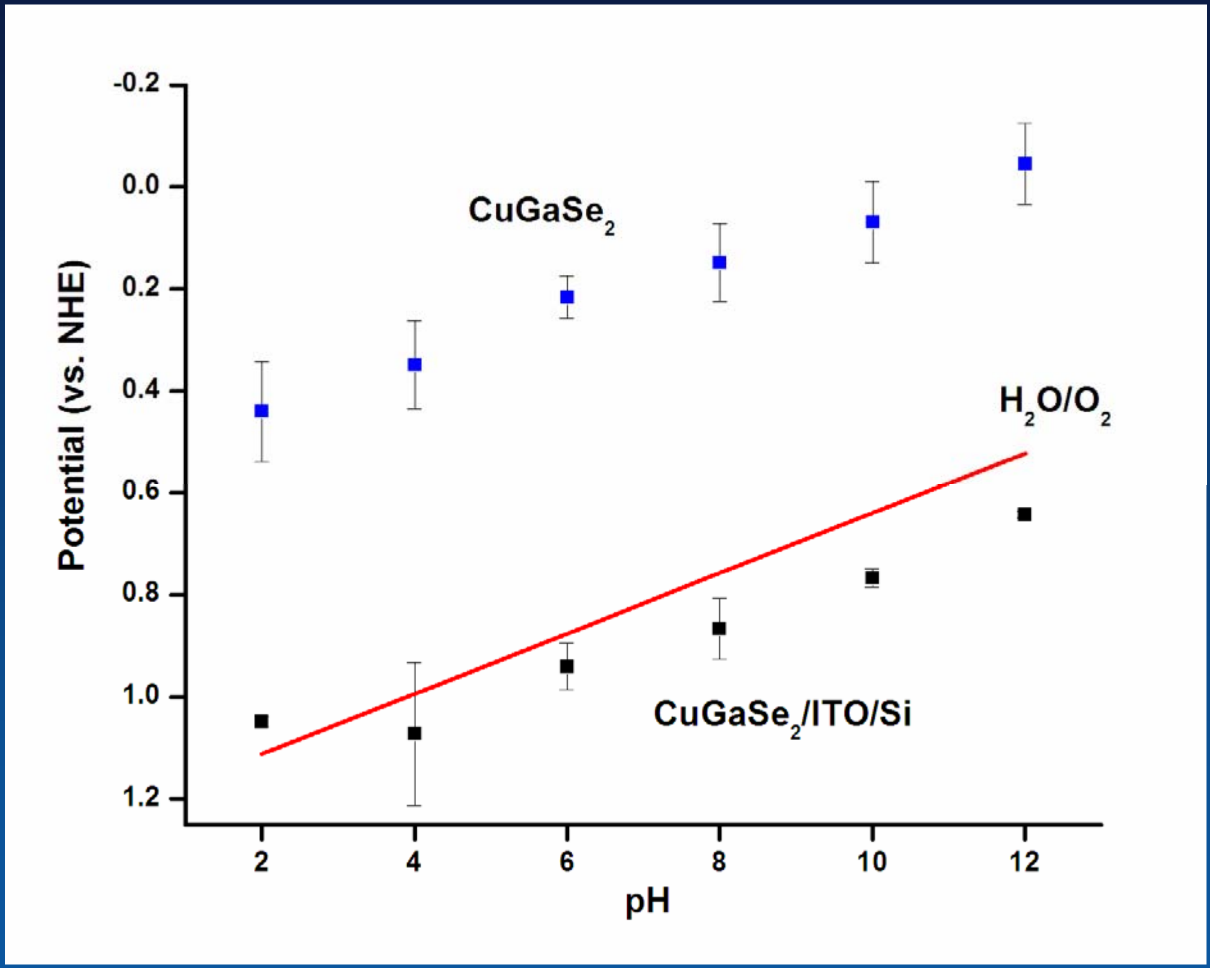
CGS Grown by Thermal Evaporation





CGS: 1.3µm
ITO: 150nm

Results – Band Positions

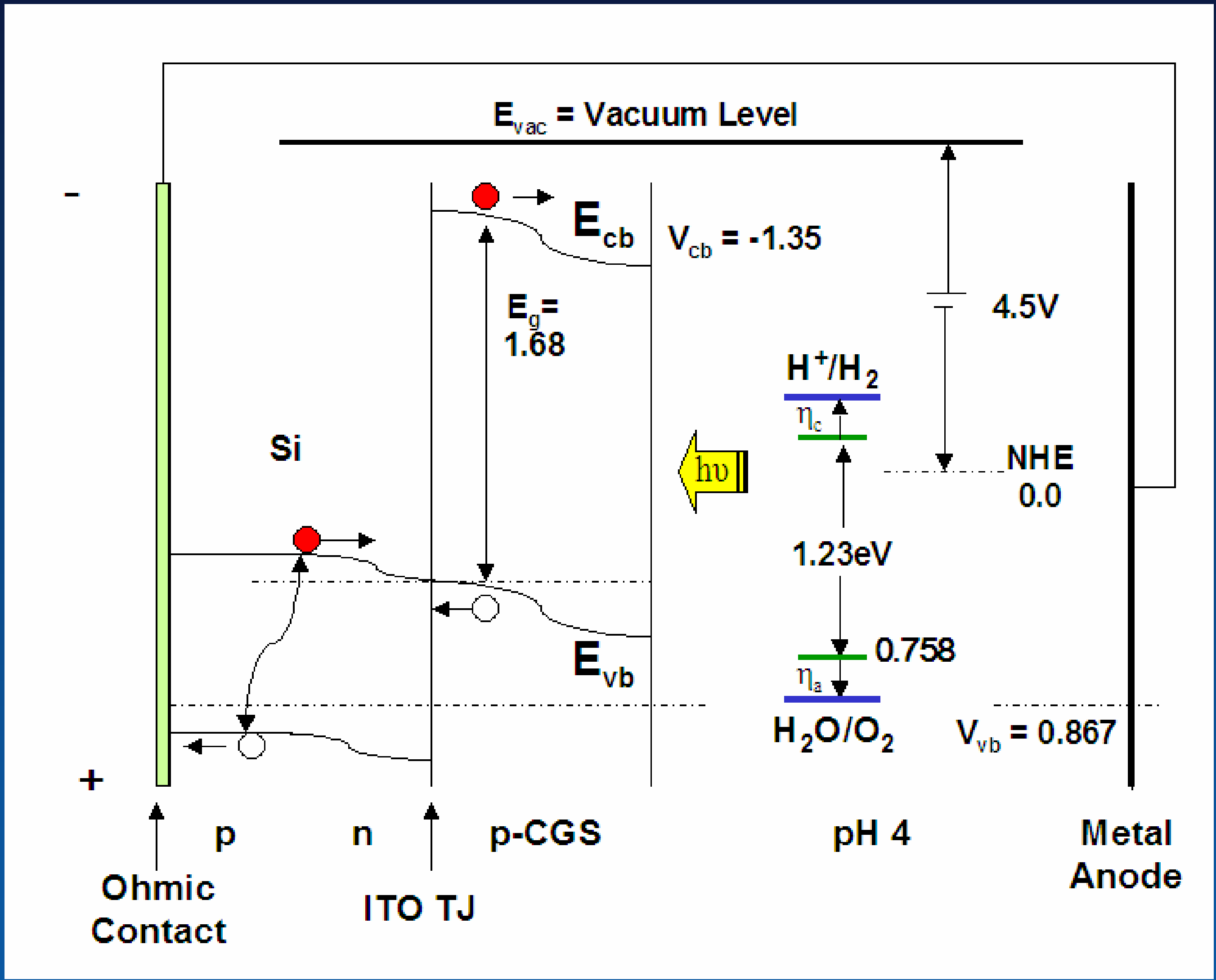


Illuminated Open Circuit Potential Measurements
High intensity DC W lamp illumination

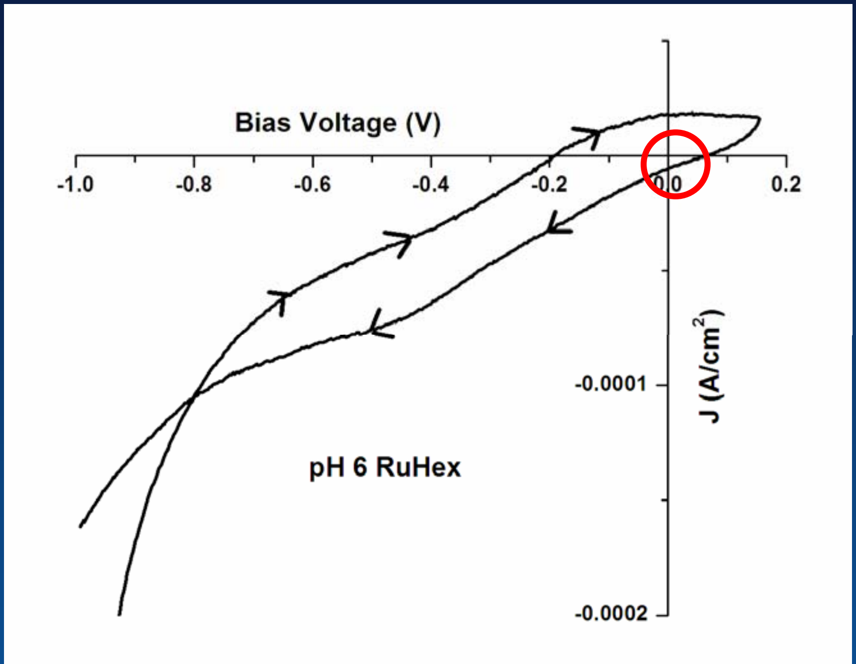
Results – Band Energy Diagram

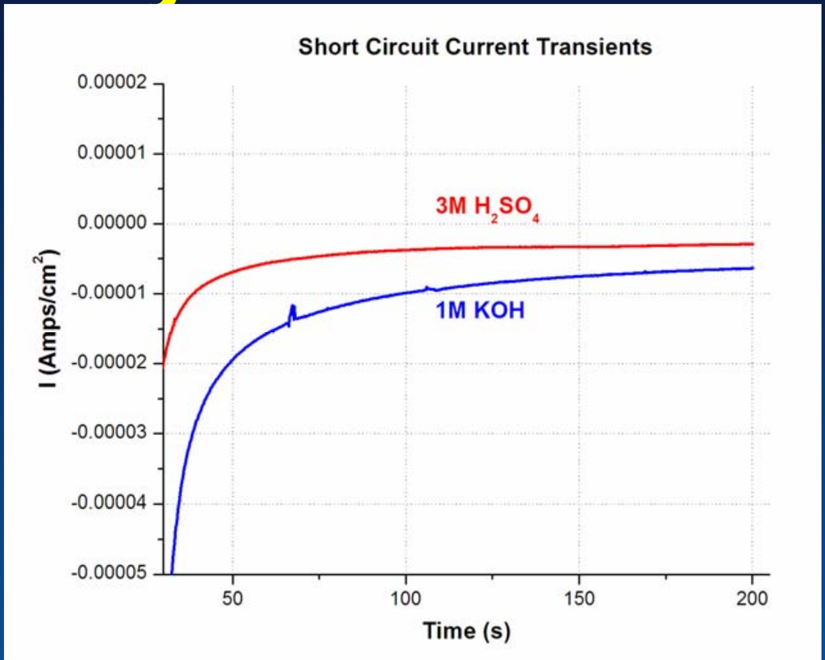
Energetics say: H_2O splitting, but very low currents

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



Results – Water Splitting Efficiency





Possible band edge alteration on anodic scan. . .

J_{SC} (Cathodic Scan)		
pH 6 RuHex, 1sun	-5.7µA	.01%
Acid, ~ 20 Suns	-3.4µA	
Base, ~ 20 Suns	-7µA	

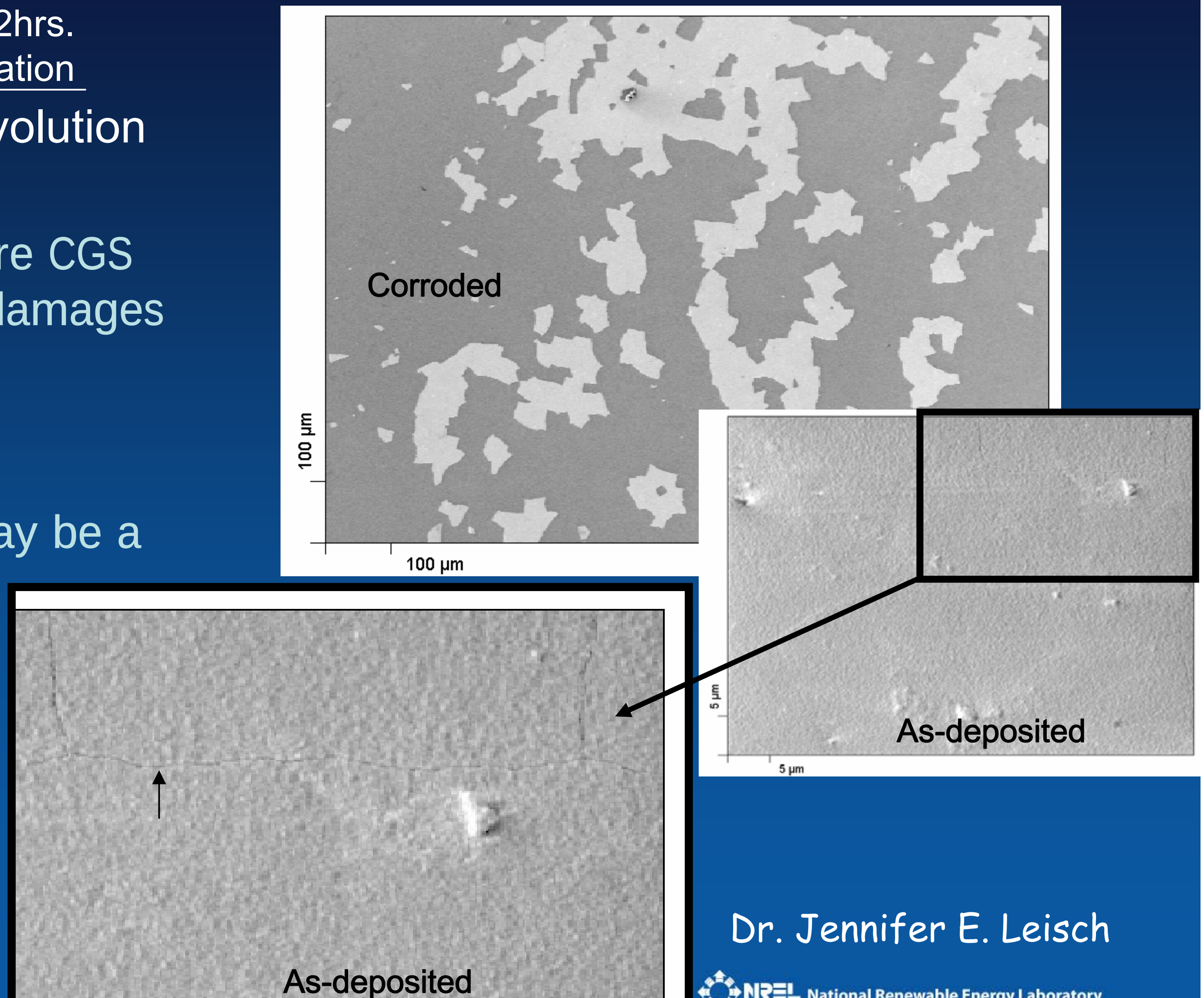
Results – Stability

2mA/cm^2, 3M H_2SO_4, 2hrs.
100mW/cm^2 W Illumination

.03mL/min-cm^2 H_2 Evolution

The high temperature CGS deposition process damages the ITO layer.

Electrodeposition may be a better approach.



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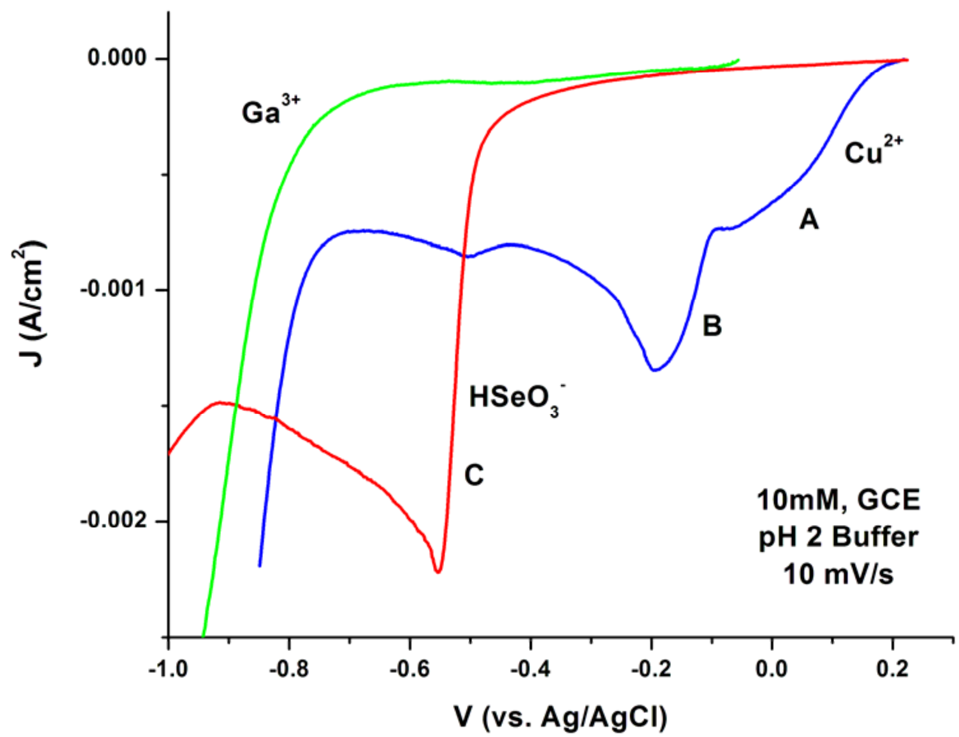
$CuGaSe_2$ Electrodeposition



$$Cu^{2+} + 2e^- \Leftrightarrow Cu \qquad E^0 = +0.342V$$

$$Ga^{3+} + 3e^- \Leftrightarrow Ga \qquad E^0 = -0.549V$$

$$H_2SeO_3 + 4e^- + 4H^+ \Leftrightarrow Se + 3H_2O \qquad E^0 = +0.739V$$

Lincot, D., et al., *Chalcopyrite thin film solar cells by electrodeposition.* Solar Energy, 2004. **77**(6): p. 725-737.

Film Microstructure

Phases Present in XRD Patterns

Cu:Ga:Se	-600mV	-700mV	-800mV	-900mV	-1000mV	-1100mV
1:10:0.5	$Cu_{2-x}Se$					
1:10:1	CuSe					
1:10:1.5	CuSe, Cu_3Se_2	CuSe, Cu_3Se_2				
1:10:2	CuSe, Cu_3Se_2	CuSe, Cu_3Se_2	CuSe, Cu_3Se_2	CuSe, Cu_3Se_2	CuSe, Cu_3Se_2	CuSe

XRD

No Ga-containing phases observed

Film Composition by ICP-MS

(inductively coupled plasma-mass spectrometery)

Cu:Ga:Se	-0.6V	-0.7V	-0.8V	-0.9V	-1.0V	-1.1V
1:10:0.5						
Cu (%)	41.86					
Ga (%)	32.68					
Se (%)	25.45					
1:10:1						
Cu (%)	33.18					
Ga (%)	30.71					
Se (%)	36.11					
1:10:1.5						
Cu (%)	39.03	32.06				
Ga (%)	1.76	21.73				
Se (%)	59.22	46.21				
1:10:2						
Cu (%)	37.14	33.32	33.69	31.85	35.47	27.00
Ga (%)	0.84	1.15	2.00	0.87	1.12	18.27
Se (%)	62.02	65.52	64.31	67.28	63.41	54.72

- **Films close to the proper stoichiometry (1:1:2) were electrodeposited (ambient T and P)**
- **Gallium deposition can be obtained via codeposition mechanism**
- **Ga must be amorphous or of very small structure**
- **Excess Se inhibits Ga deposition**
- **Next step: Annealing**

Dr. Jennifer E. Leisch

School of Mines 1874 Colorado

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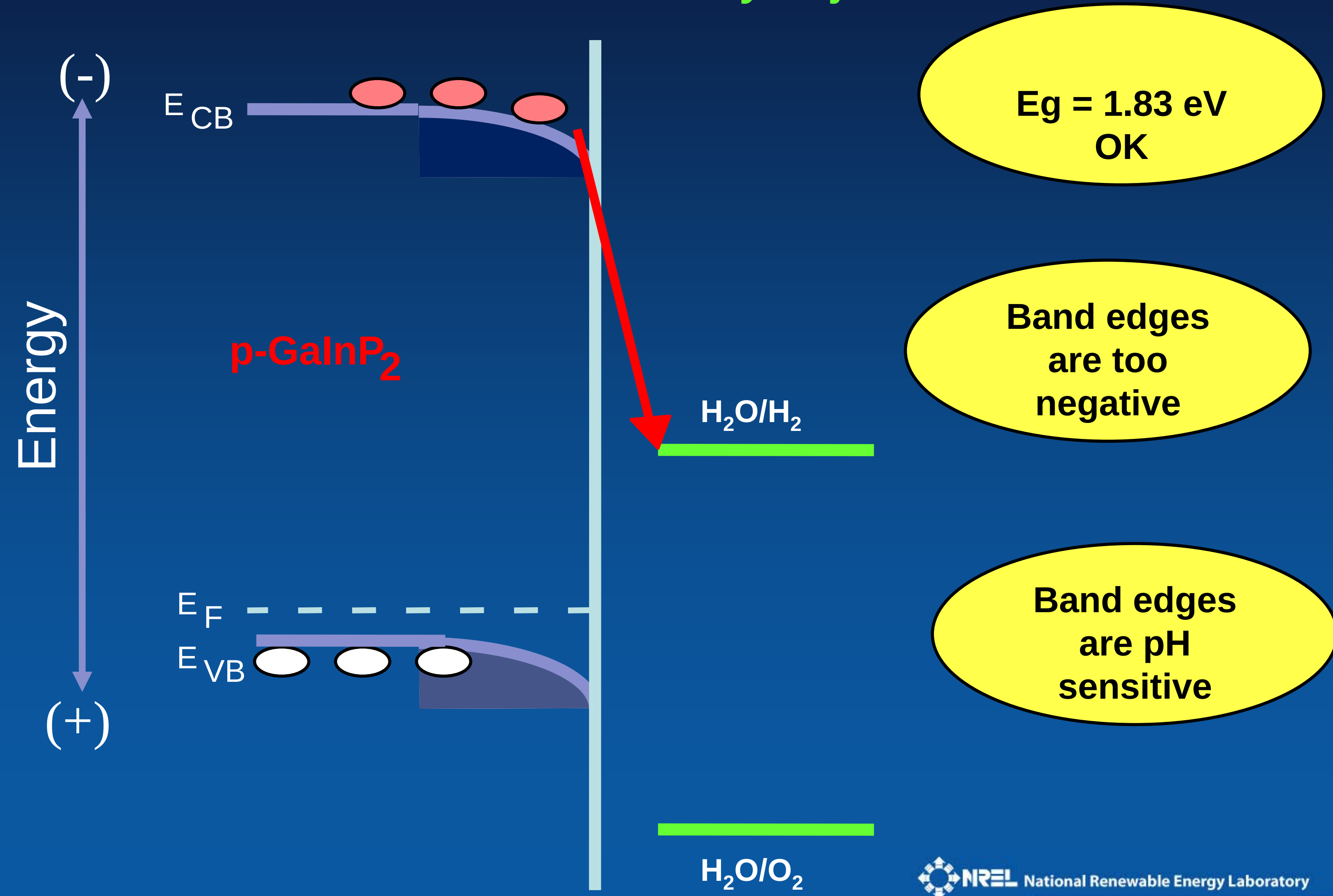
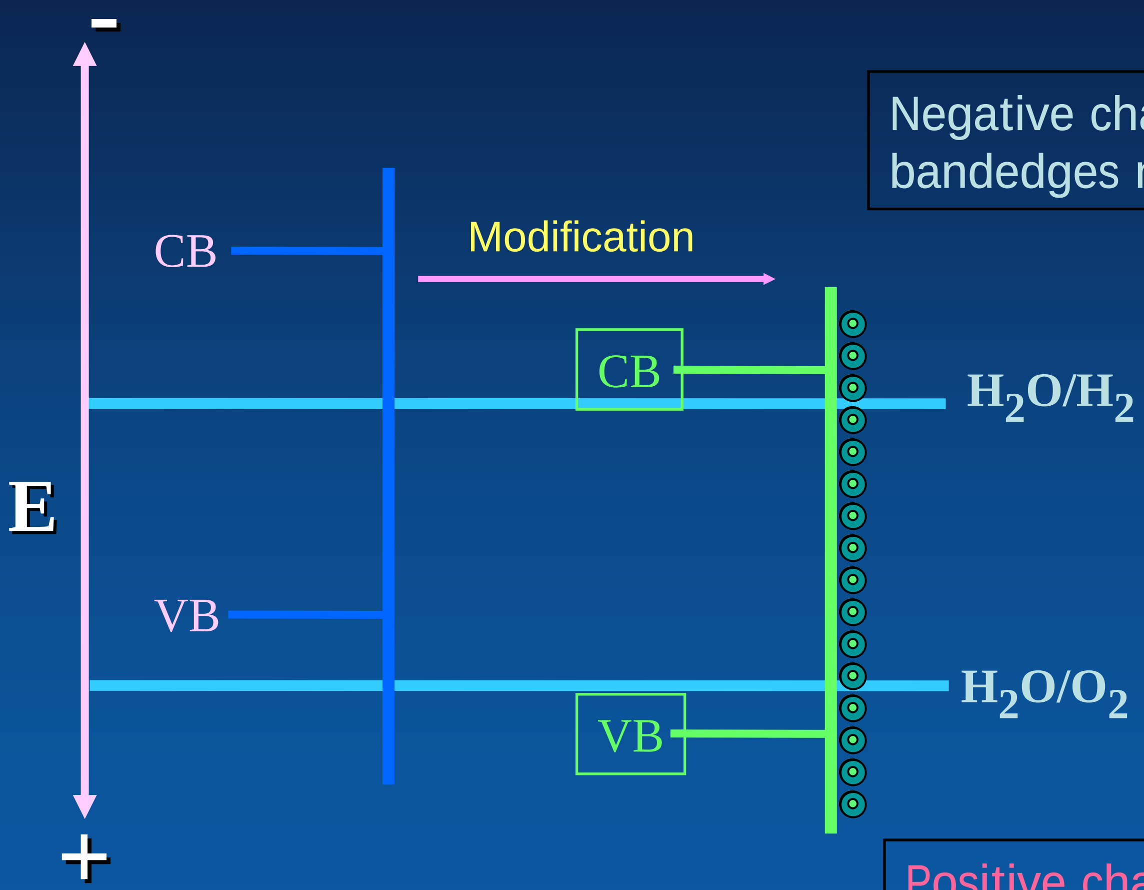
Gallium Indium Phosphide/Electrolyte System

Used to gain a fundamental understanding of semiconductor/electrolyte junctions

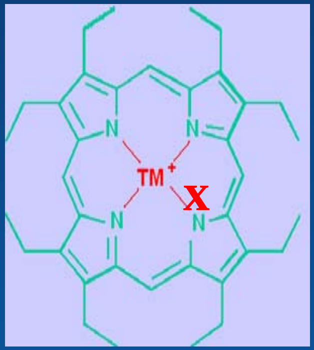


Band Edge Engineering

The goal is to shift the band edges by surface modification to provide the proper energetic overlap.

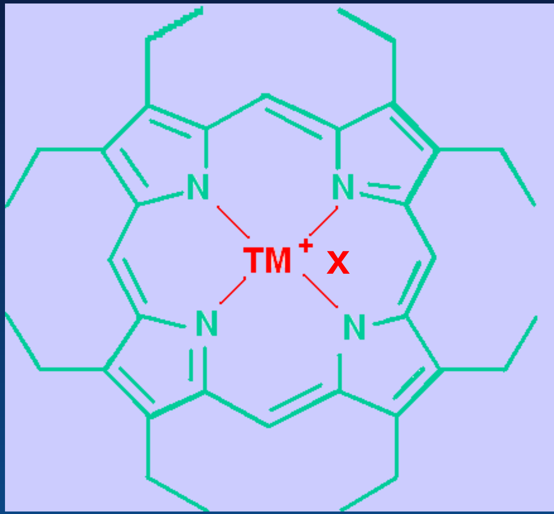


Negative charges move the bandedges negative.



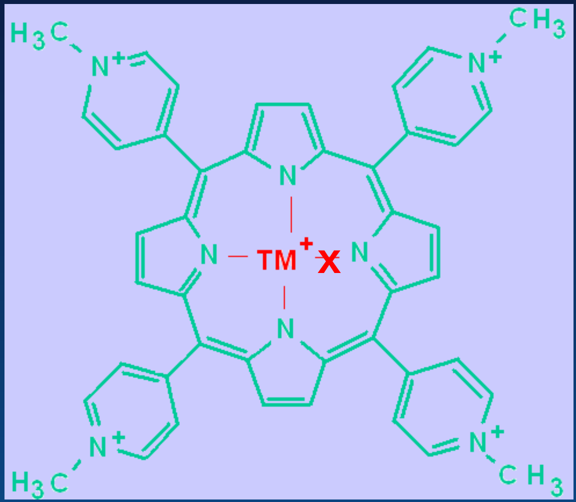
Positive charges move the bandedges positive.

Metallo-Porphyrins



Octaethyl Porphyrin

~OEP~



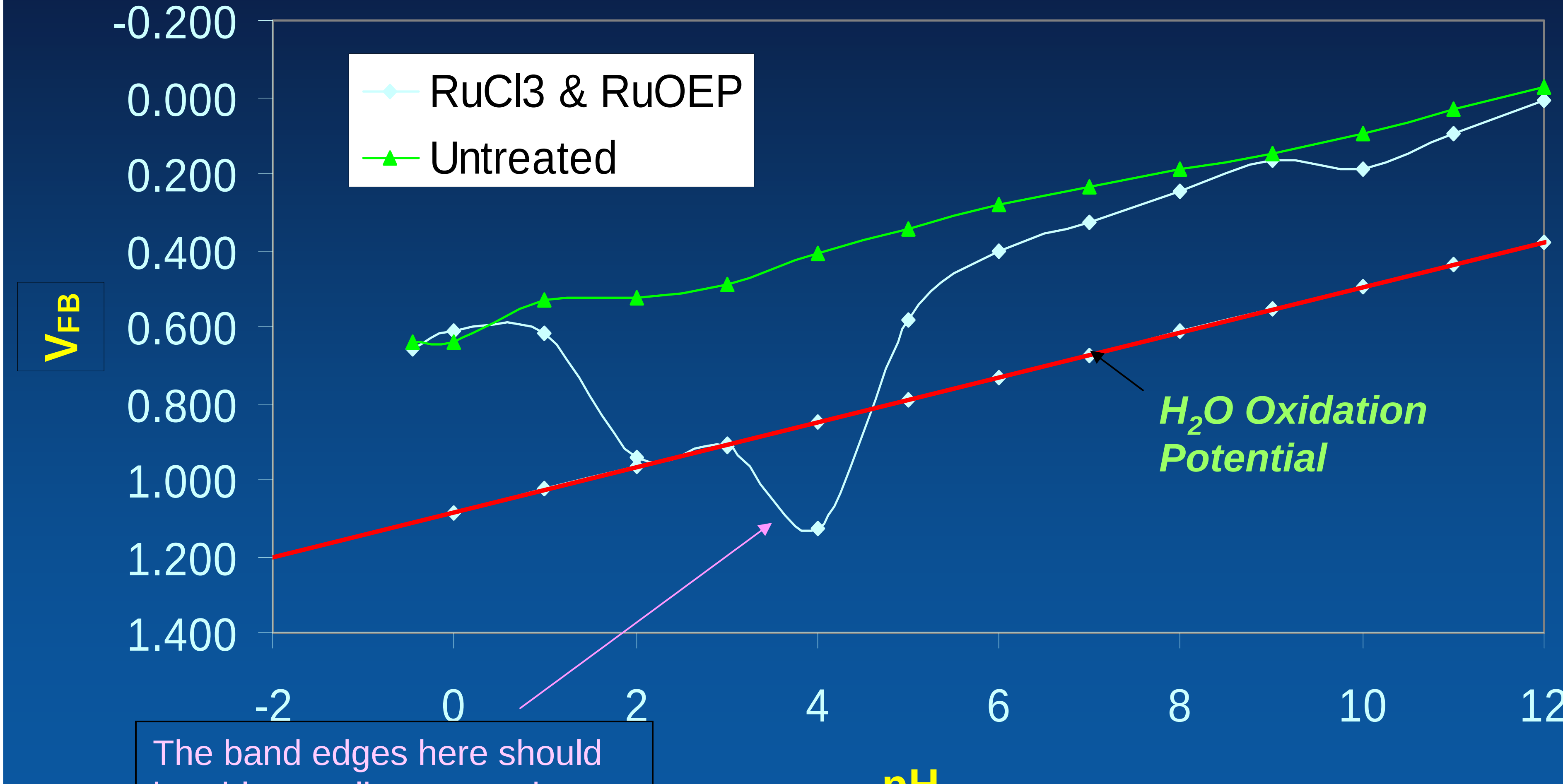
Tetra(N-Methyl-4-Pyridyl)porphyrin

~TMPyP(4)~

Insoluble porphyrin dissolved in methlene chloride and electrode coated by drop evaporation. Water soluble porphyrin applied by soaking the electrode in a solution of the porphyrin.

Band Edge Engineering - $GaInP_2$

V_{FB} vs. pH for $RuCl_3$ + RuOEP Treated $GaInP_2$ Electrode



The band edges here should be able to split water…..but no water splitting observed.

S. Warren and J. Turner, *USDOE Journal of Undergraduate Research*, p 75 (2002)

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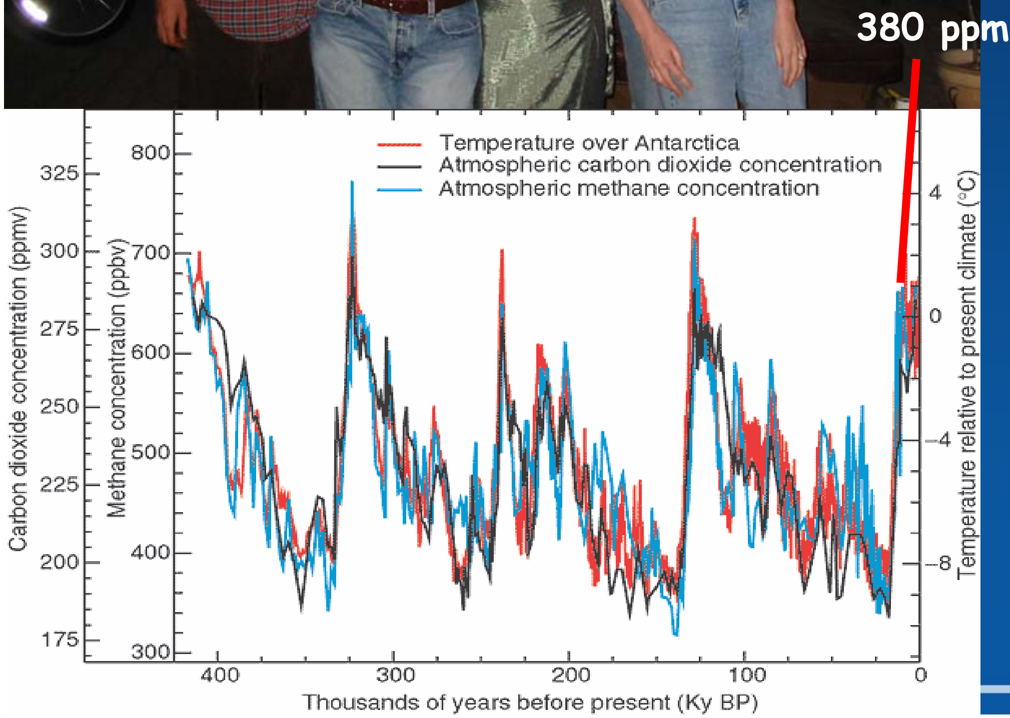
Photoelectrochemical Water Splitting



Current Staff

Heli Wang

Todd Deutsch, Postdoc

Mark Reimann, Colorado School of Mines (PhD Student)

Recent Past

Jennifer Leisch , Colorado School of Mines (PhD 2006 – now at Stanford)

Jeff Head, Colorado State University (SS- now at ASU)

Paul Vallett, University of Vermont (SS)

Scott Warren, Whitman College (SS - now at Cornell)

Others

Vladimir Aroutiounian, University of Yerevan, Armenia (CRDF, ISTC)

Arturo Fernández, Centro de Investigación en Energía-UNAM, Mexico

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