NREL National Renewable Energy Laboratory

Innovation for Our Energy Future

Photoelectrochemical Water Splitting

2008 DOE Hydrogen, Fuel Cells, and Infrastructure Technologies Program Review

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DOE Hydrogen Program

Project ID # PD36

This presentation does not contain any proprietary, confidential, or otherwise restricted information

Overview

Timeline

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

Barriers

Barriers addressed

- Y. Materials Efficiency.
- Z. Materials Durability.
- AB. Bulk Materials Synthesis.
- AC. Device Configuration Designs.

Budget

- Total project funding to date
  - DOE share: $7.0M
- Funding received in FY 2007: $800k
- Funding for FY 2008: $2000k

Partners

Interactions/collaborations

- UNLV-SHGR
- University of Nevada, Reno
- Colorado School of Mines
- University of Colorado
- Program production solicitation
  - MVSystems, Inc
  - Midwest Optoelectronics

Objectives

- **The objective of this work is to discover and characterize a semiconductor material set or device configuration that (i) splits water into hydrogen and oxygen spontaneously upon illumination, (ii) has a solar-to-hydrogen efficiency of at least 5% with a clear pathway to a 10% water splitting system, (iii) exhibits the possibility of 1000 hrs stability under solar conditions and (iv) can be adapted to volume-manufacturing techniques.**

- **The main focus of our work this past year has been to develop and optimize state-of-the-art materials that we have identified as promising for meeting DOE's near-term efficiency and durability targets.**

Table 3.1.10. Technical Targets: Photoelectrochemical Hydrogen Production [a]

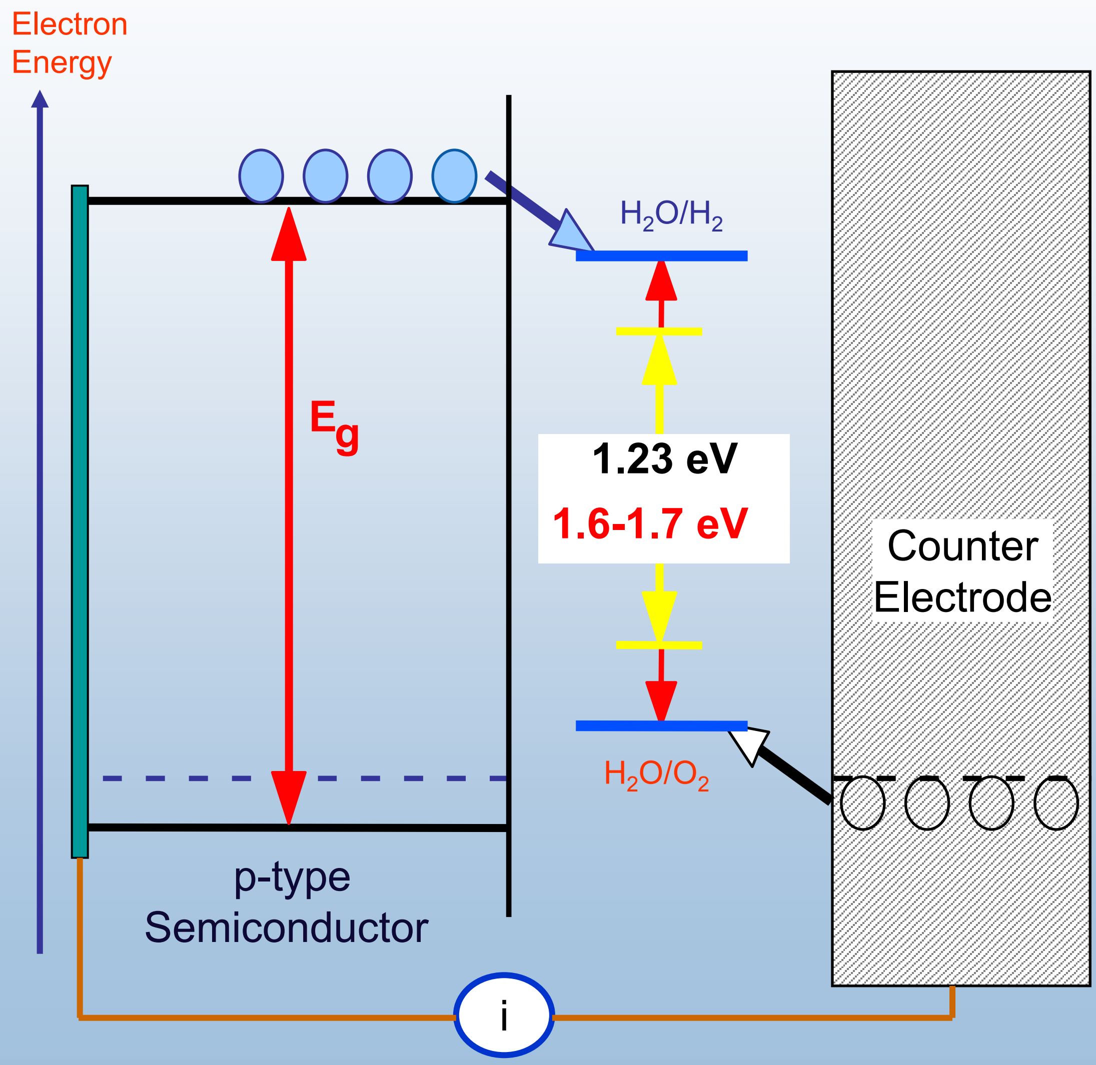
Characteristics	Units	2003 Status	2006 Status	2013 Target	2018 Target [b]
Usable semiconductor bandgap [c]	eV	2.8	2.8	2.3	2.0
Chemical conversion process efficiency (EC) [d]	%	4	4	10	12
Plant solar-to-hydrogen efficiency (STH) [e]	%	not available	not available	8	10
Plant durability [f]	hr	not available	not available	1000	5000

Milestones

	Milestones	Completion Date
3.4.1	Complete experiments on the water-splitting efficiency of a system based on GaInPN nitride material, either as a single material or as a tandem cell	08/08
3.4.2	Complete initial characterization of SiN for direct water splitting and as coating for a-Si, and go-no-go decision for additional studies	09/08
3.4.5	Complete initial study of corrosion testing to estimate stability of improved single-phase CIGSSe material for application to a tandem cell	09/08

Material Challenges *(the big three)*

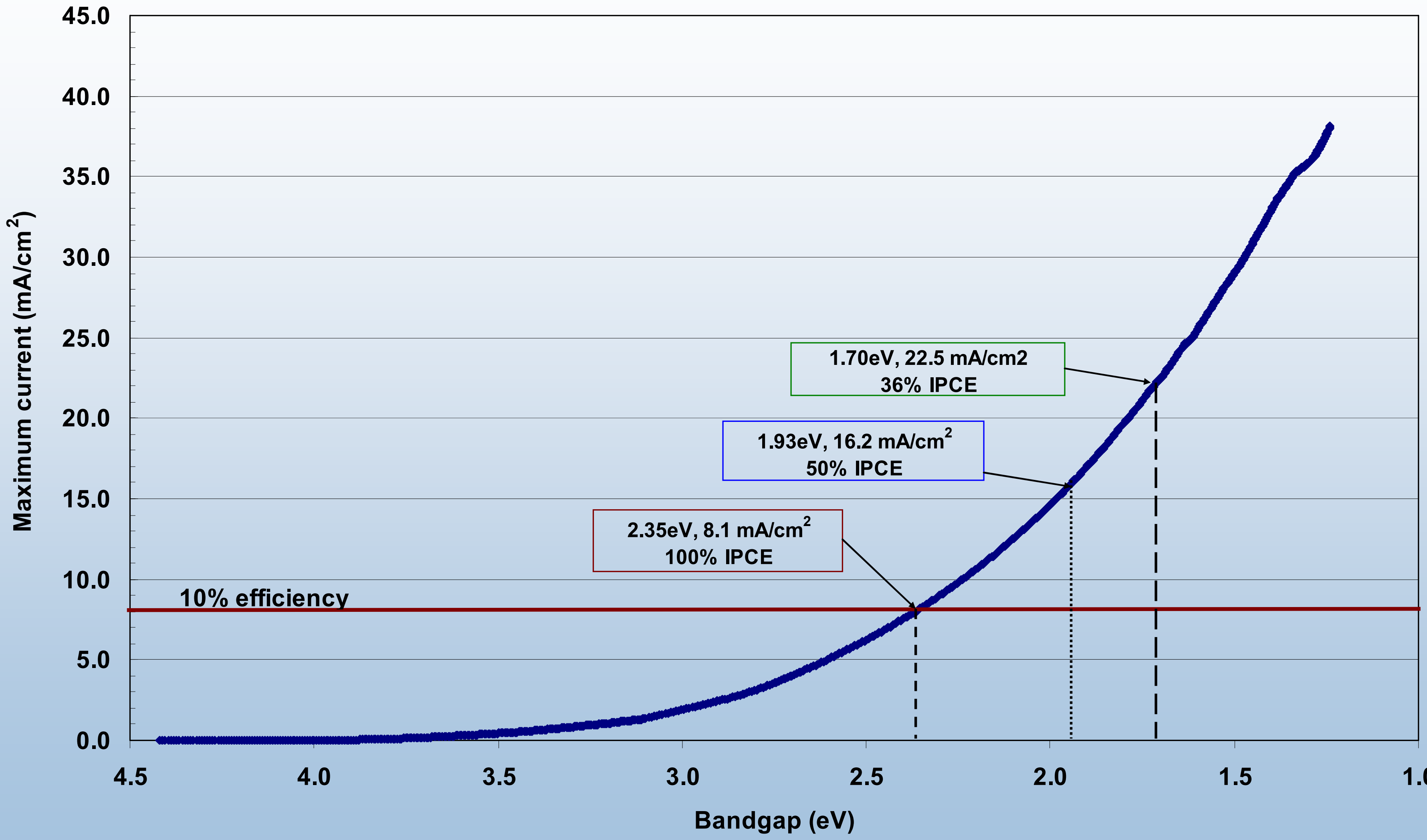
Characteristics for Ideal Photoelectrochemical Hydrogen Production Material



- **Efficiency –** 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 –** band edges must straddle H_2O redox potentials (Grand Challenge)

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

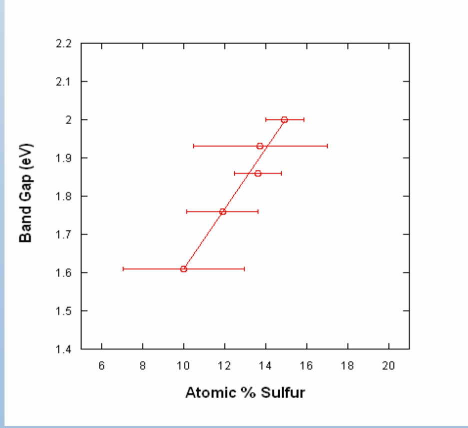
Maximum Current vs. Bandgap for AM 1.5



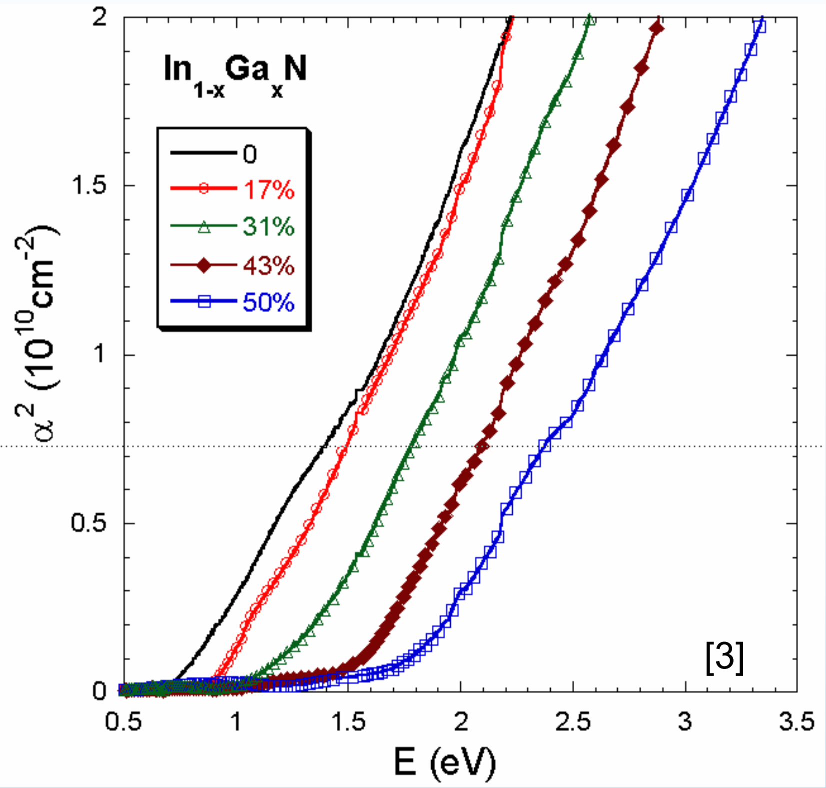
Approach
Materials: High Efficiency, Mixed Metal Oxides & Low-Cost Manufacturing

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 (0.7eV – 3.4 eV)
    - 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
- Other thin-film materials with good characteristics
  - SiC: low-cost synthesis, stability
  - SiN: emerging material
- Mixed Metal Oxides
  - Theory
  - Synthesis and characterization



Alloy GaN with InN



Indium Nitride (InN)

InN demonstrates a direct E_g of 0.7 eV.[1]

Has been reported to be stable.[2]

Band edge positions unknown

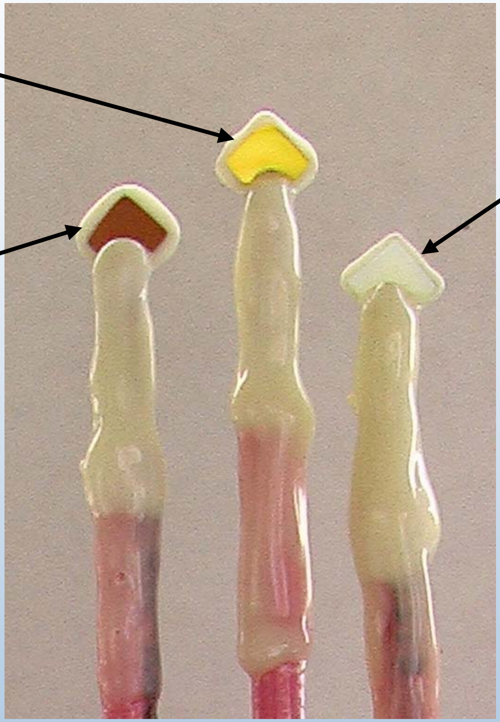
Goal: Meet three of the necessary requirements for photoelectrochemical water splitting with indium gallium nitride semiconductor ($In_xGa_{1-x}N$) alloys.

(1) Inushima, T.; Vecksin, V. V.; Ivanov, S. V.; Davydov, V. Y.; Sakon, T.; Motokawa, M. *J. Cryst. Growth* **2001**, *481* (1), 227–228.

(2) Bhuiyan, A. G.; Hashimoto, A.; Yamamoto, A. *Appl. Phys. Rev*. **2003**, *94* (5), 2779–2807.

(3) J. Wu, W. Walukiewicz, K.M. Yu, J.W. Ager III, E.E. Haller, Hai Lu, and William J. Schaff, APL, 80, p4741 **2002** (http://www.osti.gov/energycitations/purl.cover.jsp?purl=/799591-nLuLXr/)

Indium Gallium Nitride Alloy Materials under Investigation



Nominal compositions

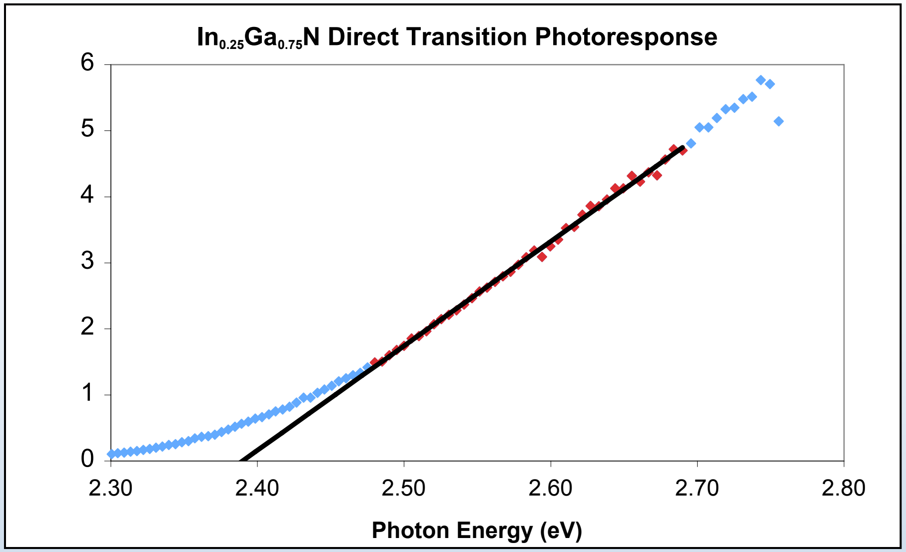
The sample wafer was cleaved into fourths, mounted to a copper wire using silver paint and coated with epoxy

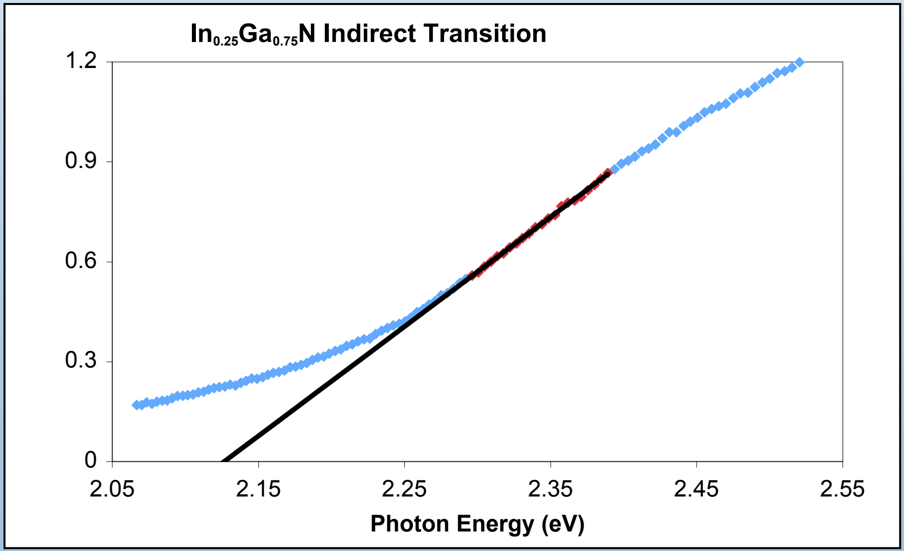
All samples were grown by molecular beam epitaxy, have indium ohmic front contacts and though nominally undoped, were determined experimentally to be n-type.

Measured Transitions for $In_{0.25}Ga_{0.75}N$ (Yellow)

Direct Transition = 2.39 eV

Indirect E_g = 2.13 eV



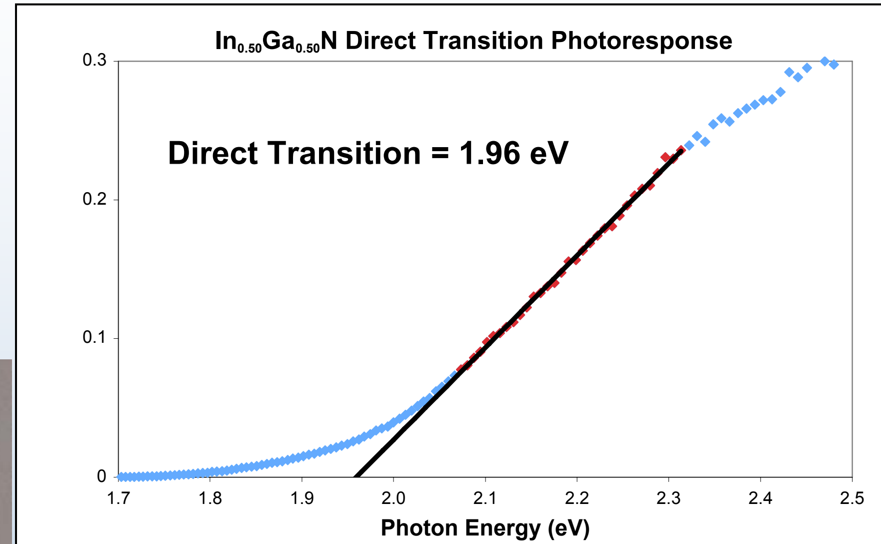


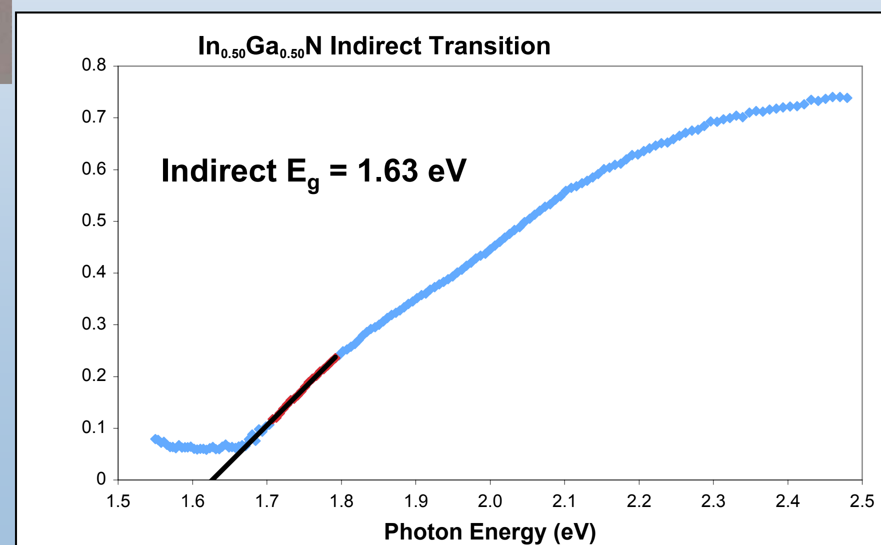
pH 2 buffer with 1mM Na_2SO_3

Measured Transitions for $In_{0.50}Ga_{0.50}N$ *(Red)*

Direct Transition (eV)
1.96
1.89
1.97

Indirect E_g (eV)
1.63
1.51
1.50

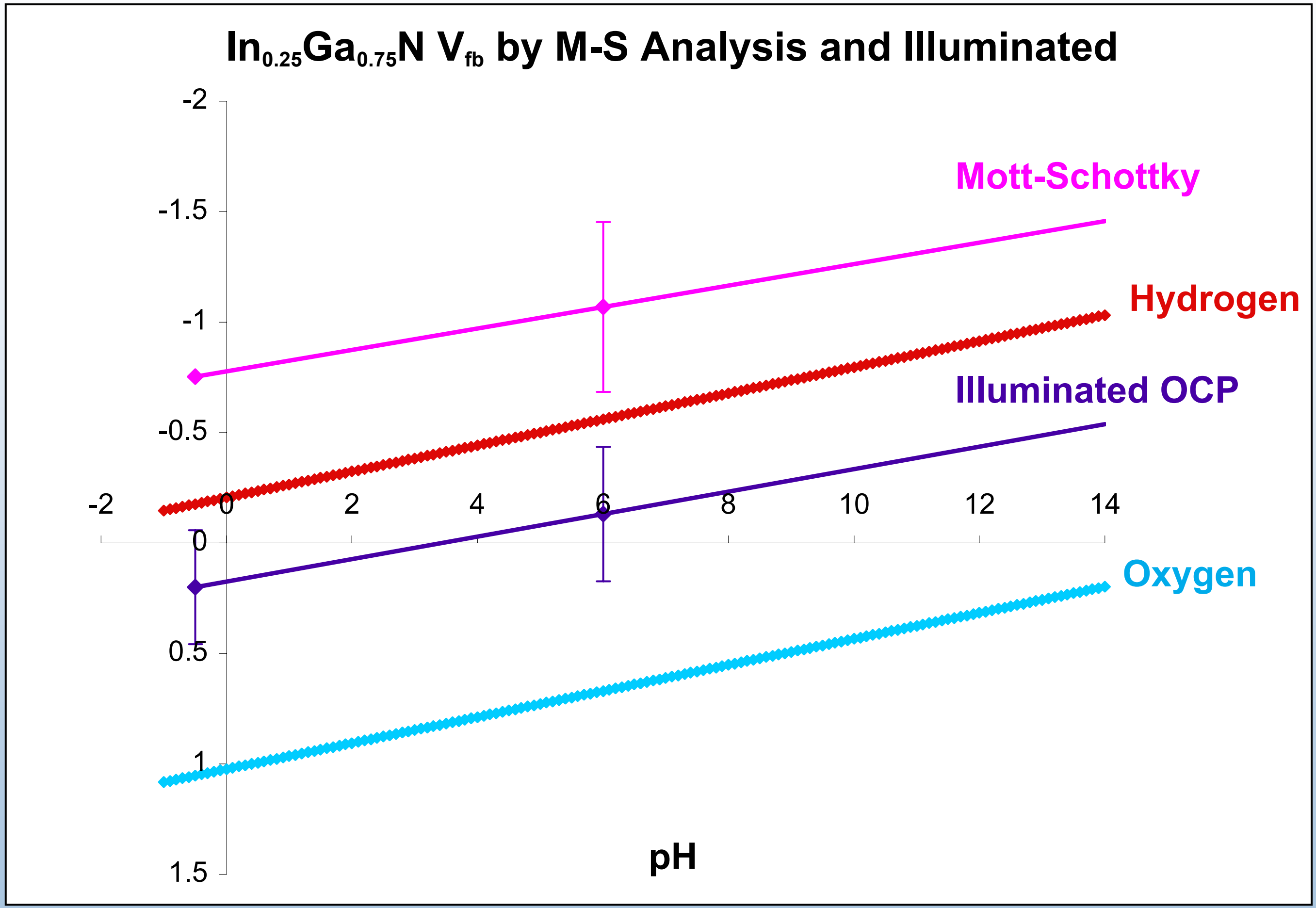




Variability observed in measured band gaps across electrodes cleaved from same sample run.

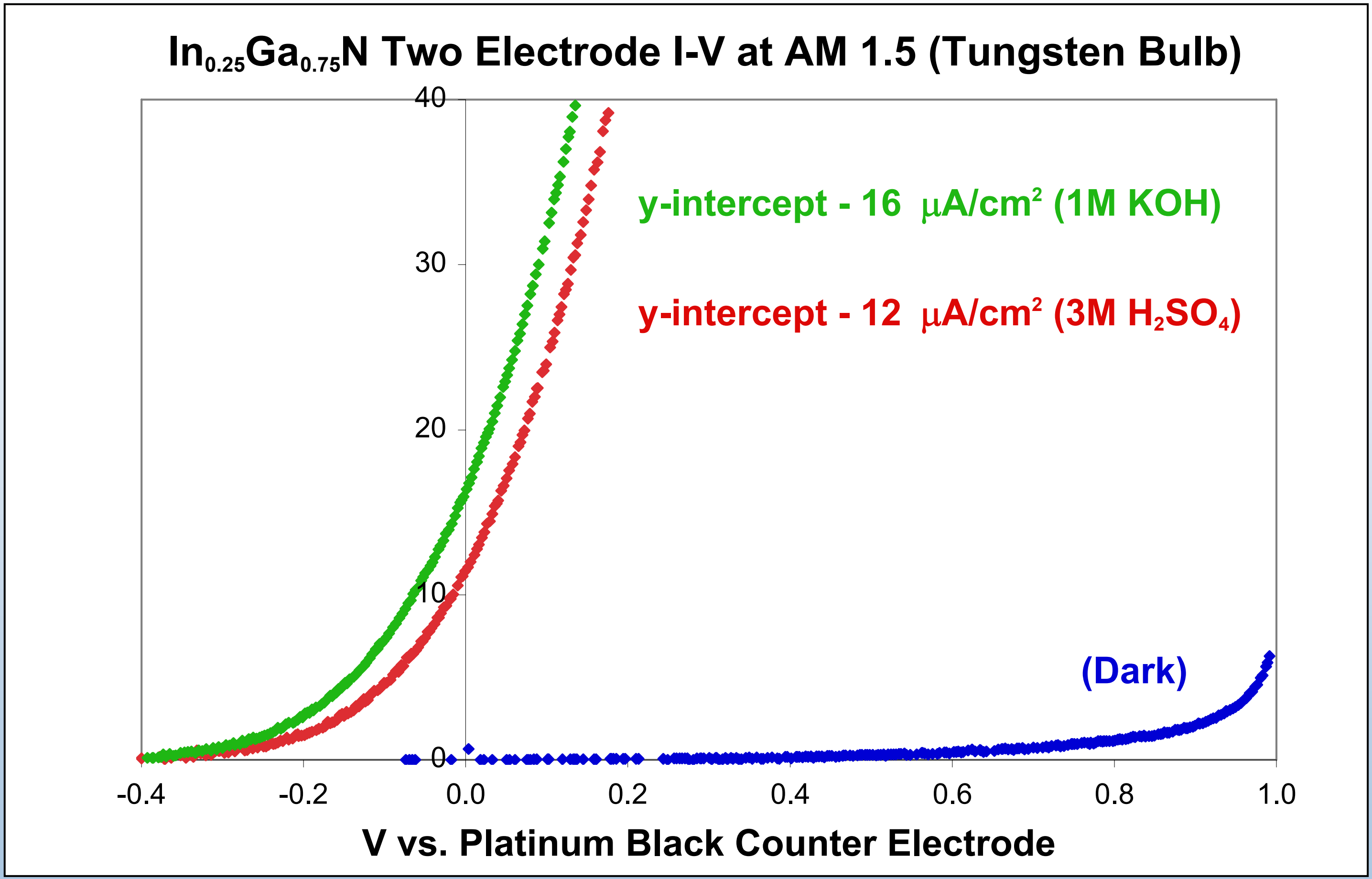
pH 2 buffer with 1mM Na_2SO_3

Flatband Potential of $In_{0.25}Ga_{0.50}N$ (Yellow)



Experimentally determined V_{fb} values were variable, and the results of various techniques lacked agreement.

$In_{0.25}Ga_{0.75}N$ Two Electrode I-V Curves *(Yellow)*

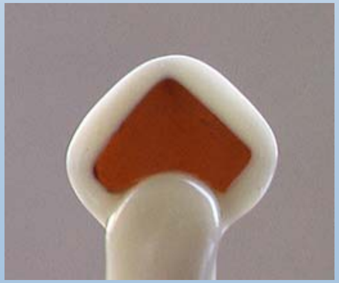


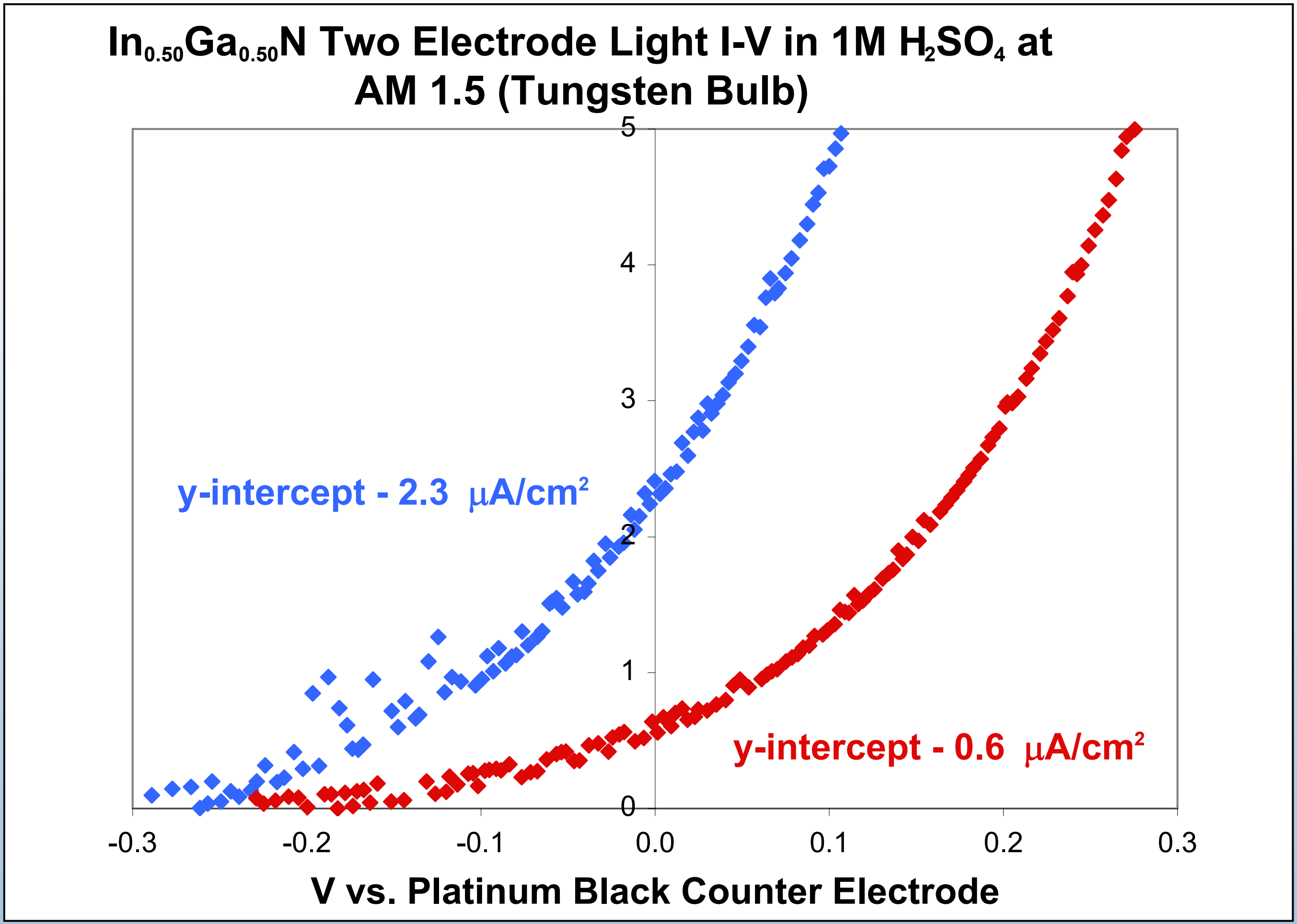
At zero applied bias there is 12–16 μA/cm² of anodic current.
(The maximum theoretical short circuit current density when E_g = 2.13 eV is 11.9 mA/cm²)

Pt Modified Surface
$In_{0.50}Ga_{0.50}N$ Two Electrode I-V Curves (Red)

Accomplishments

- Synthesis of nitride material with necessary bandgap.
- Possible single-gap water splitting system.

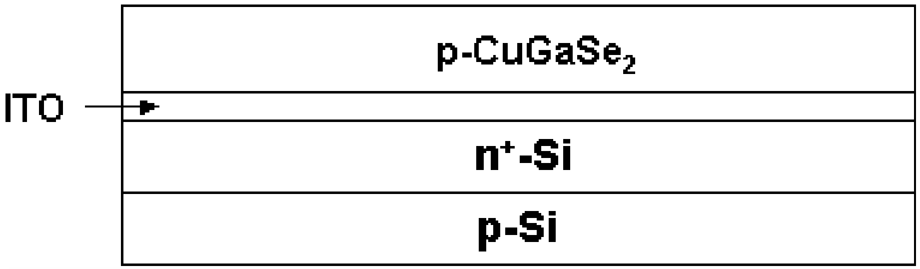


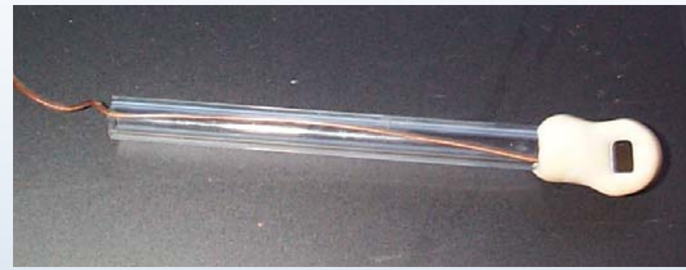


Platinum catalysis surface treatment of the electrode increased the anodic current at zero applied potential.

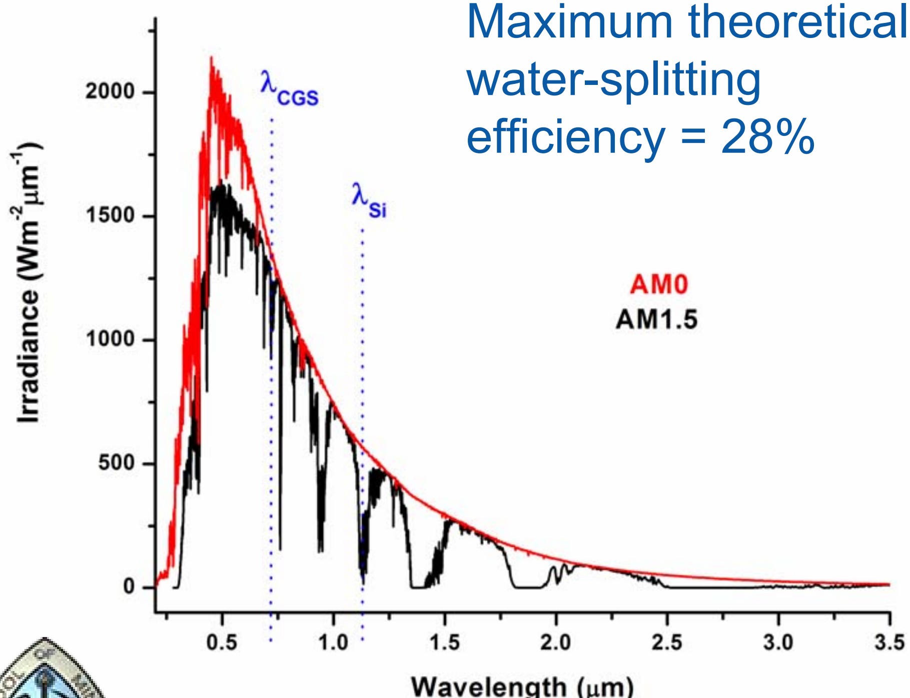
$CuGaSe_2$ Tandem Cell Configuration:

Possible High Efficiency, But a New Deposition Approach is Required

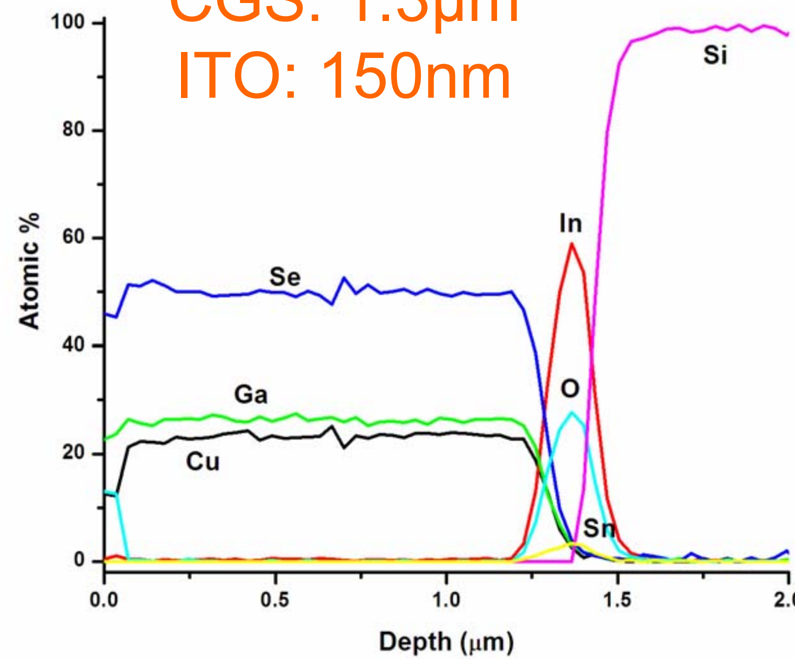




Maximum theoretical water-splitting efficiency = 28%



CGS: 1.3µm
ITO: 150nm

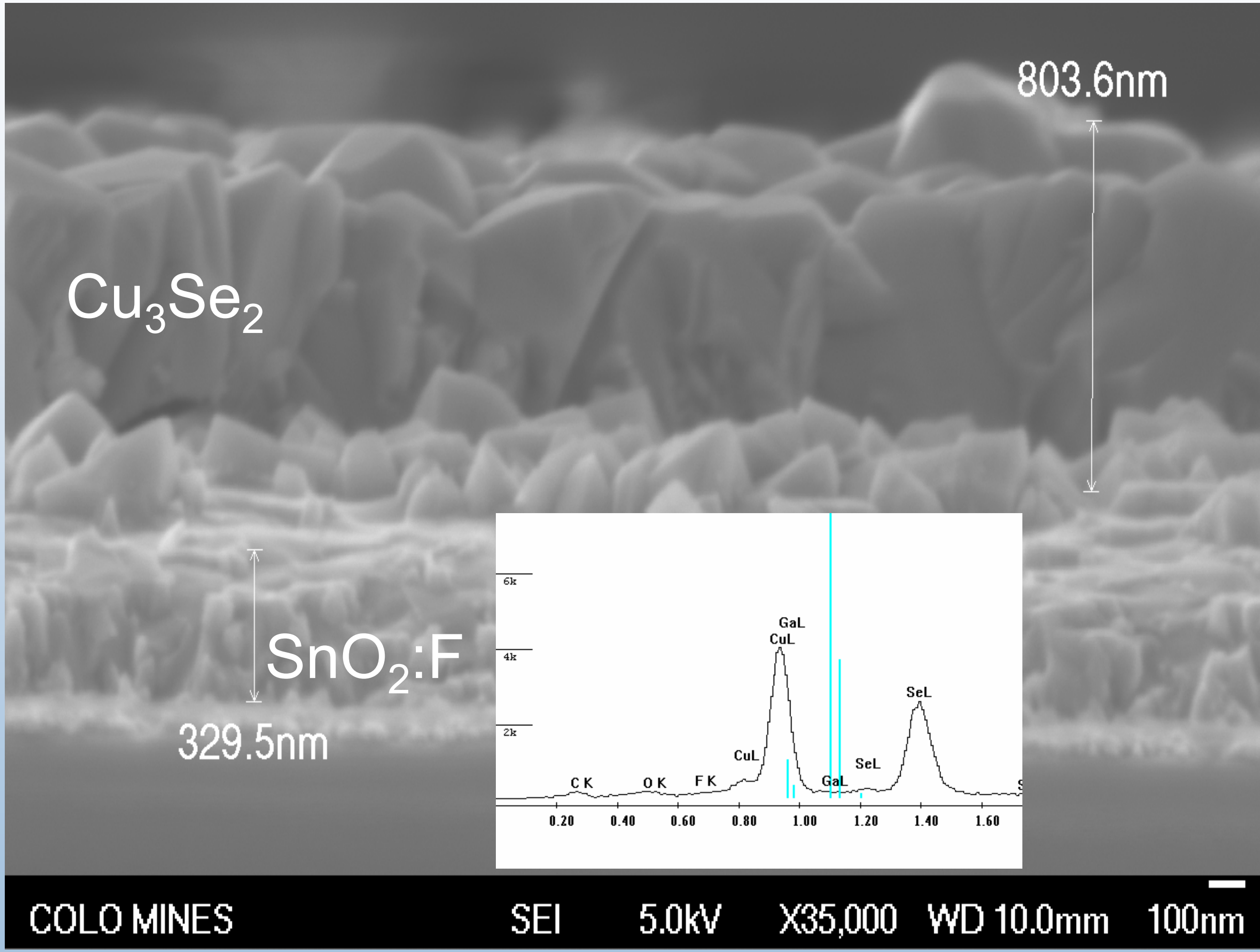


SEM Image of Electrodeposited C(G)S Thin Film

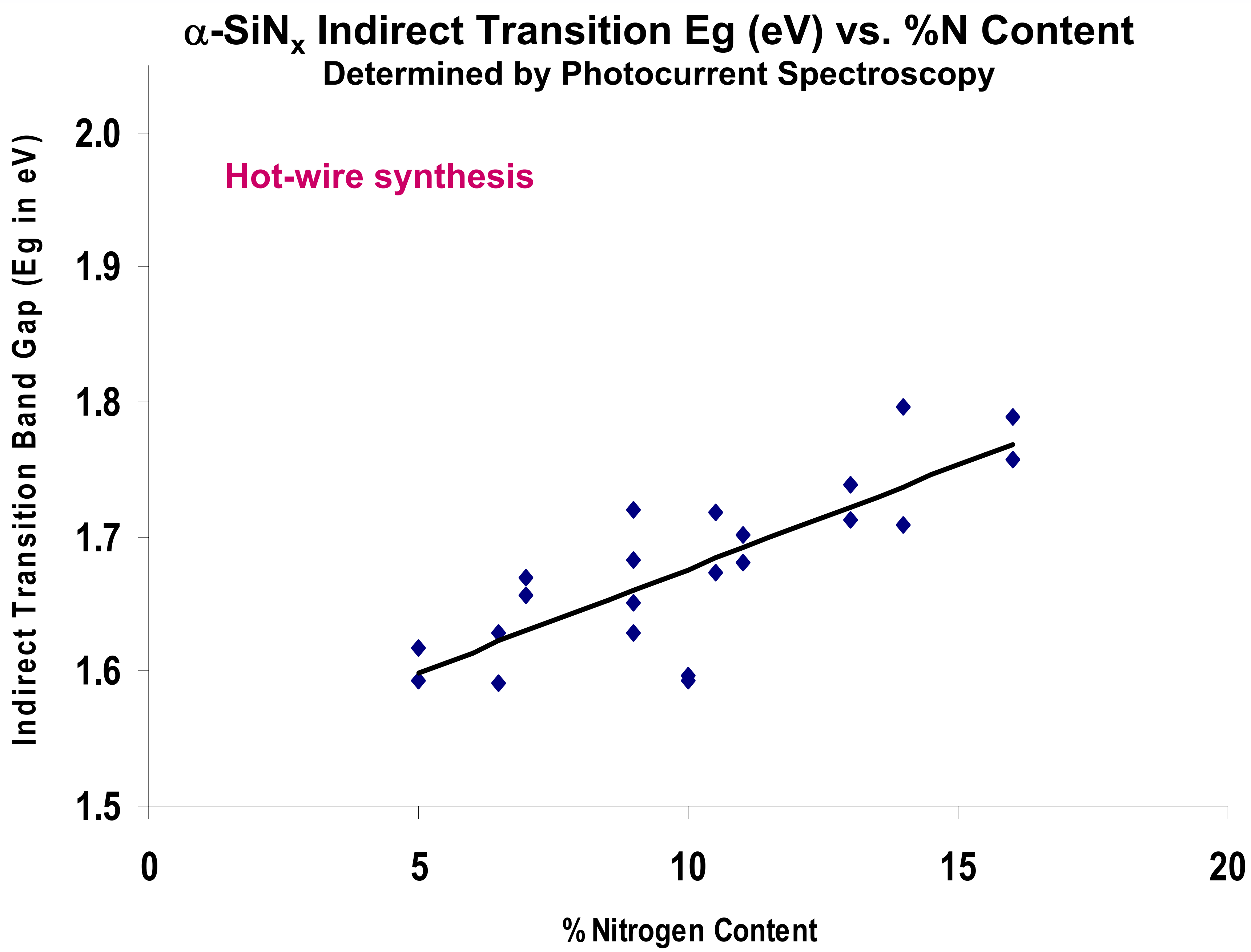
Unannealed, crystalline Cu_3Se_2 by XRD, Stoich Cu_3Se_2 by EDS

Accomplishments

- Low-temperature synthesis of crystalline material
- Electrodeposited on SnO:F
- Incorporation of Ga



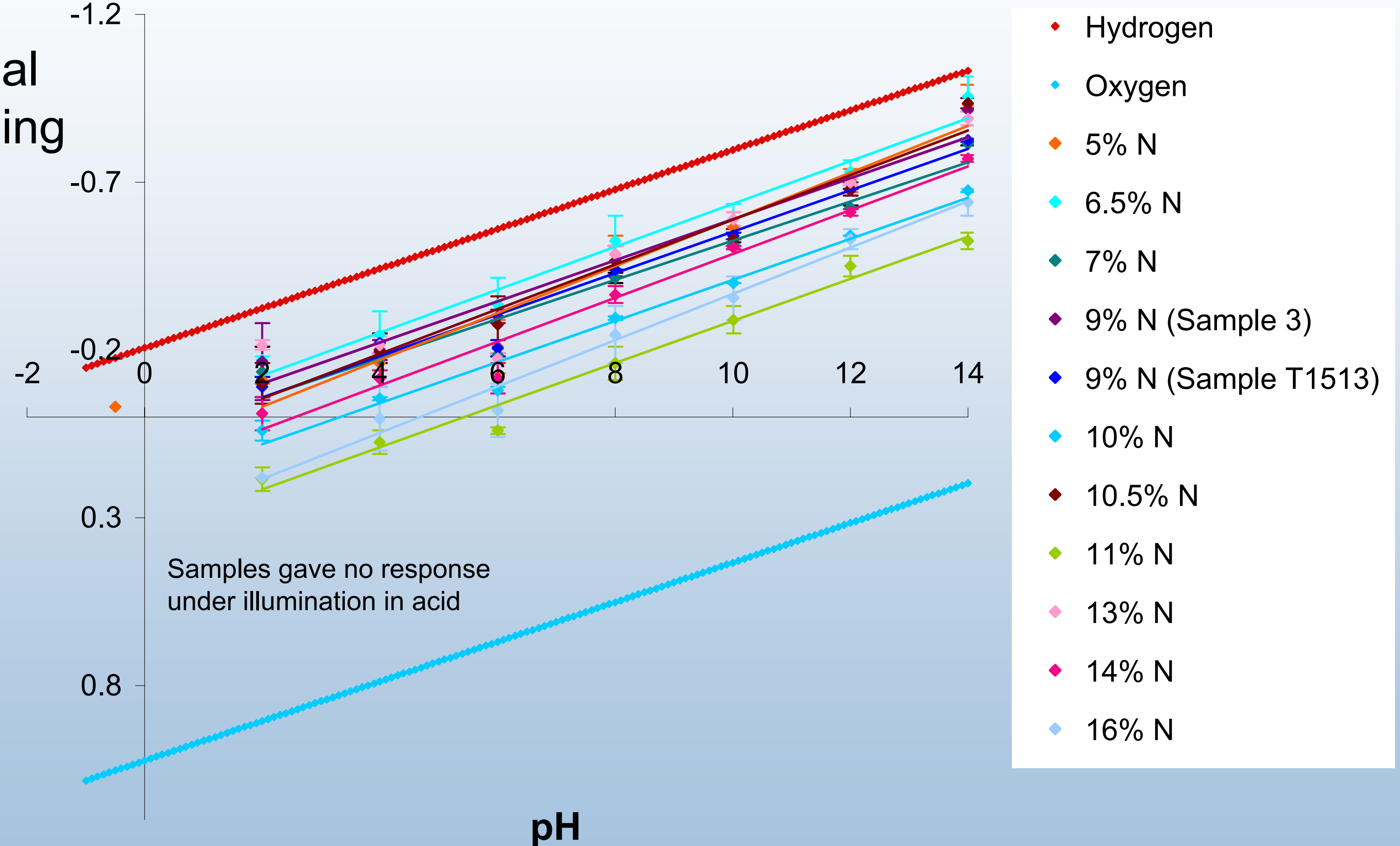
Bath is 500mL solution of 0.225g of $CuCl_2 \cdot 2H_2O$, 4.5 g $GaCl_3$, 0.450 g H_2SeO_3, and 3.0 g LiCl buffered pH = 3


α-SiNx Indirect Transition Eg (eV) vs. %N Content
Determined by Photocurrent Spectroscopy
Hot-wire synthesis
Indirect Transition Band Gap (Eg in eV)
2.0
1.9
1.8
1.7
1.6
1.5
0
5
10
15
20
% Nitrogen Content

n-SiN V_{fb} by Illuminated OCP

Accomplishments

- New material with promising bandgap
- Low-cost synthesis approach



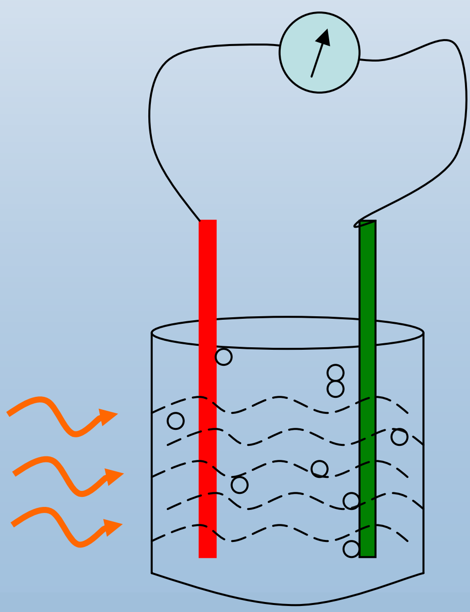
Metal Oxides: An approach to achieving fundamental PEC goals

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

- There are no PV devices based on metal oxides
- Metal oxides typically have low absorption coefficients (at least the ones with color), low carrier mobilities and short diffusion lengths - a perfect storm of poor semiconductor properties.
- There are easily 50,000 combinations of ternary oxides and over 2 million quaternary oxides.
  - Any material search must rapidly achieve a fundamental understanding of the limiting factors of the current material sets and then identify alloy combinations that can address these limitations.
- A collaboration of theory, synthesis, and characterization groups is necessary to achieve fundamental PEC goals.
  - The key will be the predictive capability of the theory groups coupled with the synthesis capability of the growth groups.
  - The right questions are needed

Theory of Oxides for Photoelectrochemical Hydrogen Production - Poster

R&D feedback loop



Project ID #
PDP34

Co-Fe-Al Oxide System (VI)

- The drawback of cobalt spinels is the weak absorption in the visible range arising from the nature of the d-d optical transitions.

- To overcome these limitations we are currently investigating isovalent cation substitution.
- Based on changes in the electronic energy levels on transition from Al to Ga to In, we predict a dramatic increase in visible light absorption.

- **Experimental verification of these predictions are in progress.**

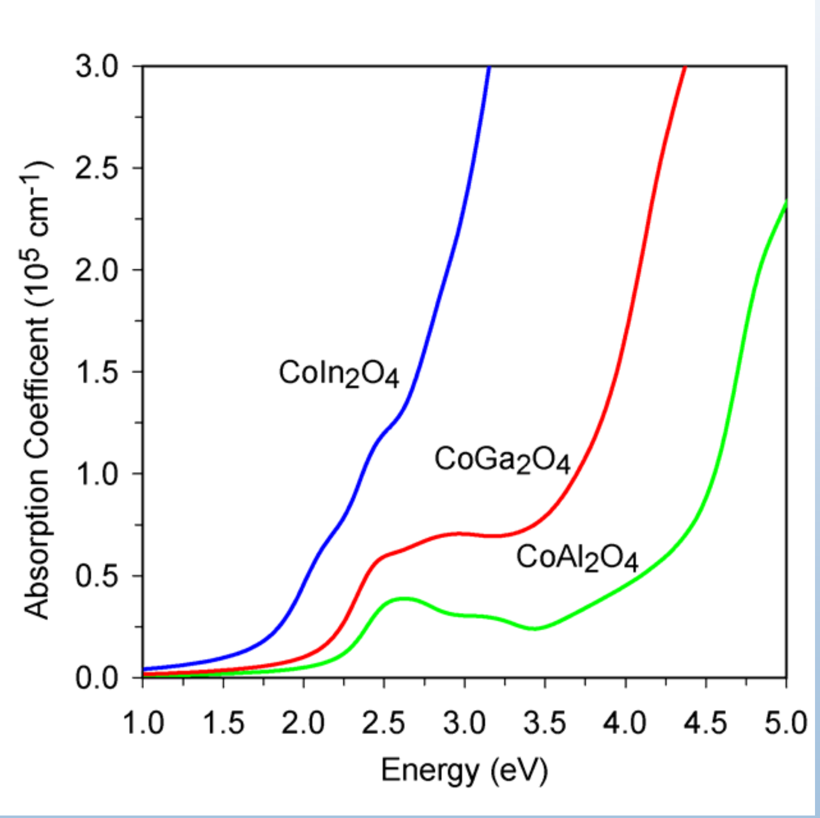
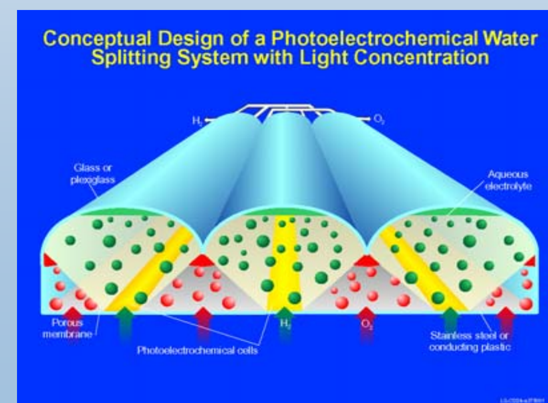


Figure: Calculated absorption spectra.

Future Work

- Continue to study GaInN materials and explore low-cost synthesis approaches.
- Explore other III-V nitride analogs, e.g. ZnSnN
- Complete study of electrodeposited $CuGaSe_2$ materials.
- Continue characterization of SiN materials.
- Explore new mixed metal oxides - theory, synthesis and characterization.
- Support other members of the PEC working group.

R&D feedback loop



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