National Renewable Energy Laboratory
Innovation for Our Energy Future

Semiconductor Materials for Photoelectrolysis

DOE Hydrogen Program
Annual Merit Review

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Project ID#: PD035

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Overview

Timeline

- Project start date: 1991
- Project end date: 2012
- Percent complete: N/A

Budget

- Total project funding
  - DOE share: $9.8M
- Funding received in FY09: $1350k
- Funding for FY10: $1100k

Barriers

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

Partners

- Interactions/ collaborations
  - Los Alamos National Laboratory
  - University of Nevada Las Vegas
  - Colorado School of Mines
  - University of Colorado
  - University of Hawaii
  - Stanford University
  - Program production solicitation
    - MVSystems, Inc.
  - Small Business Innovation Research
    - Synkera Technologies, Inc.
    - Physical Optics Corporation

Objectives/Relevance

- 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/Relevance

FY09

	Milestones	Completion Date
3.4.1	Complete experiments on the water-splitting efficiency of a system based on GaInN nitride material.	11/09
3.4.2	Complete characterization of SiN for direct water splitting and as coating for a-Si, and go no-go decision for additional studies.	09/09

FY10

	Milestones	Completion Date
3.4.1	Complete experiments on the durability of InGaN material and estimate material lifetimes	01/10
3.4.2	Complete characterization of a-SiC coated a-Si, and report efficiency and lifetime status	01/10
3.4.3	Complete study of corrosion testing of a-SiC in collaboration with UNLV analysis and report on potential for long-term stability	04/10
3.4.4	Complete preliminary study of nitrided $GaInP_2$ and make go no-go decision on further study.	04/10
3.4.5	Complete initial testing of ALD coated $GaInP_2$ and make go no-go decision on further study	04/10
3.4.6	Complete characterization (efficiency and stability) of nanostructured MoS_2 and WS_2.	09/10
3.4.7	Complete characterization of delafossite materials and make go, no-go decision	09/10

Approach

Break down the large set of possible materials into two general categories

Non-Oxides

III-V materials have the highest solar conversion efficiency of any semiconductor material ($GaInP_2$/GaAs tandem >12% solar-to-hydrogen)

- Direct transition band gap, couple µm's of material, not 100's of µm
- Large range of available band gaps (0.7eV – 3.4 eV)
  - Stability an issue – nitrides show promise for increased lifetime (Barriers Y & Z)
  - Band-edge mismatch with known materials – tandems an answer (Barrier AC)

I-III-VI materials offer high photon conversion efficiency and possible low-cost manufacturing–Cu(In,Ga)(S,Se)

- Synthesis procedures for desired band gap unknown (Barrier AB)
- Tandem on Si p/n, requires low-temp synthesis

Other thin-film materials with good characteristics

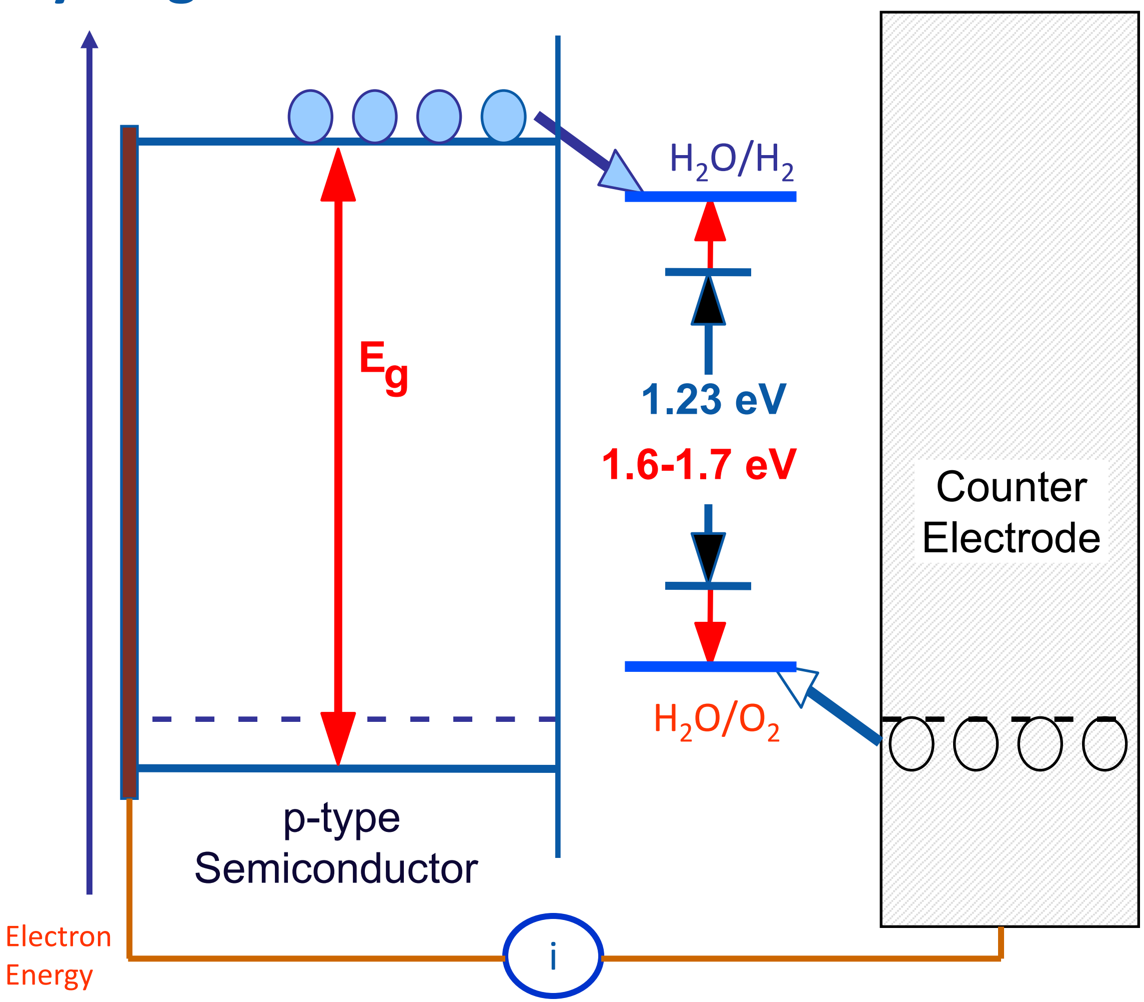
- a-Si/a-SiC: low-cost synthesis, stability (Barrier AB)
- a-SiN: emerging material (Barrier AB) no-go

Mixed Metal Oxides

- Theory-DFT calculations to identity promising candidates
- Synthesis and characterization
- Cu, Bi, Sb based ternary or multinary oxides

Material Challenges *(the big three)*

Characteristics for Ideal Photoelectrochemical Hydrogen Production Material



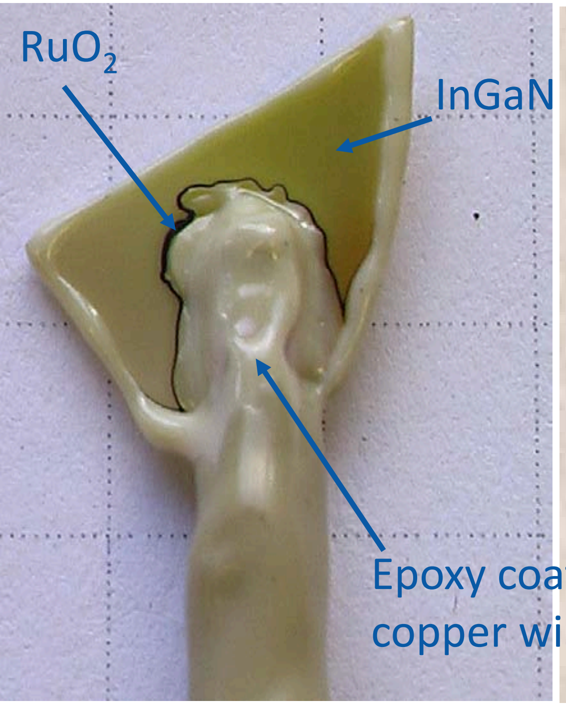
- **Efficiency –** band gap (E_g) must be at least 1.6-1.7 eV, but not over 2.2 eV; must have high photon to electron conversion efficiency
- **Material Durability –** semiconductor must be stable in aqueous solution
- **Energetics –** band edges must straddle H_2O redox potentials (Grand Challenge)

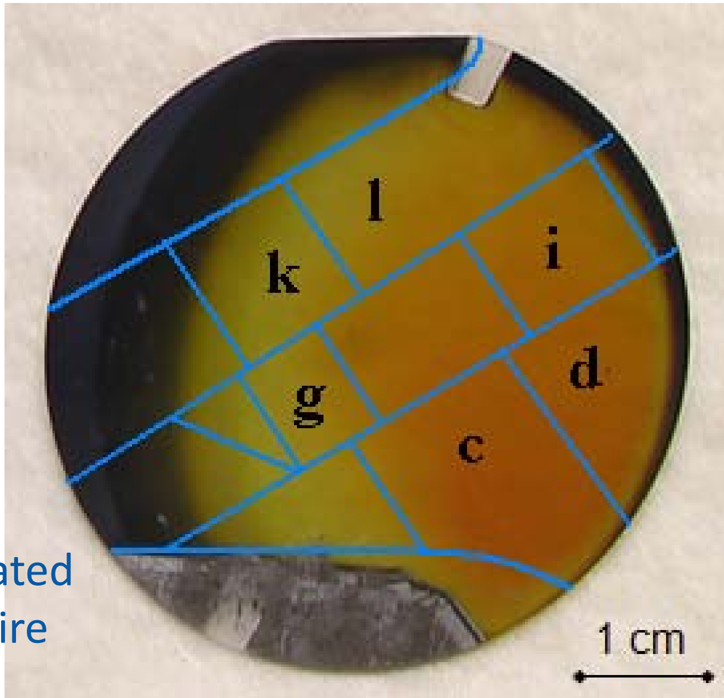
All must be satisfied simultaneously.

Technical Accomplishments and Progress

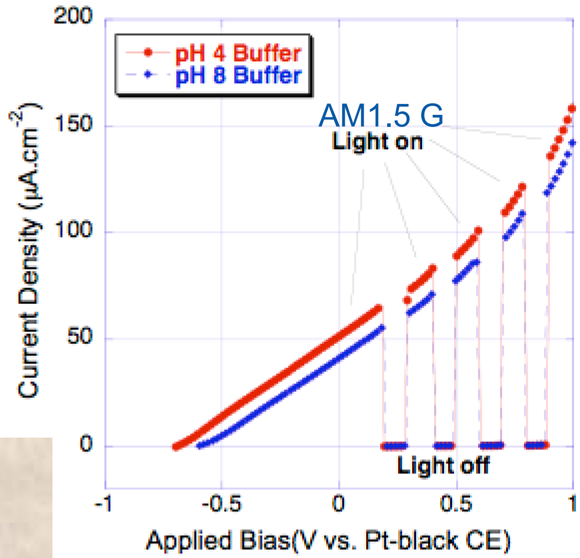
$In_xGa_{1-x}N$: III-V Nitride Materials (Los Alamos)

- Electroplating of Ru from $RuCl_3$ solution for O_2 evolution catalysis demonstrate deficiency in contact geometry for LANL InGaN
- Contact issues prohibit realistic catalyst, durability, efficiency studies
- Photocurrents (efficiency) could be improved by several orders of magnitude

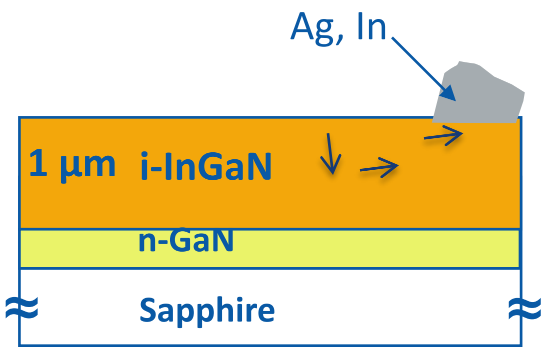




Unbiased water splitting



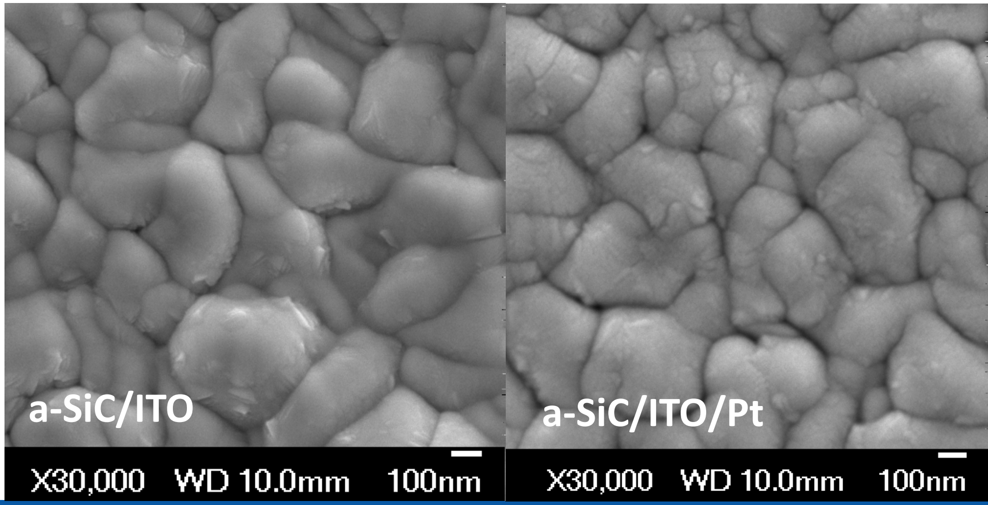
Low efficiency
(poor carrier collection)



Technical Accomplishments and Progress

a-Si & a-SiC thin films

- p-type photocathode materials
- a-SiC is forming insulating SiOx layer at electrolyte interface severely hindering short-circuit current
  - PEC a-Si/a-SiC hybrid <1mA/cm^2
  - Solid-state analogue ~5mA/cm^2
- HF etch improved short-circuit current, but maximum value (1.3 mA/cm^2) still well below solid-state value
- Continued durability testing of a-SiC
  - Results are highly variable
- Series of hybrid/tandem cells capped with ITO to prevent SiOx formation were tested
  - Thick layer of capping Pt sputtered on top (more like PV/electrolysis than PEC)
  - Electrodes degraded faster than bare a-SiC

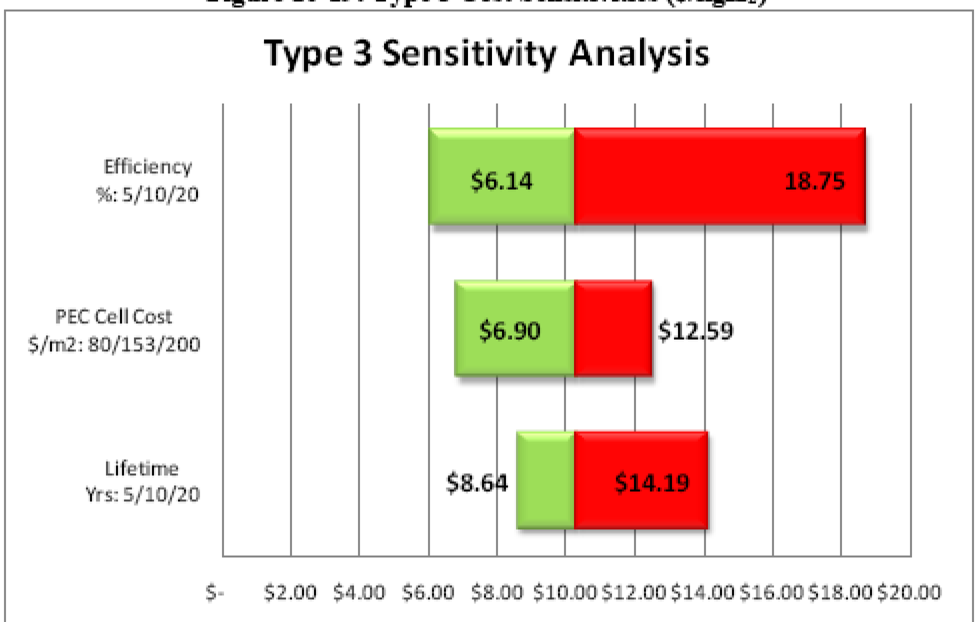


Technical Accomplishments and Progress

CuGaSe$_2$ (CGS) Durability (Univ. of Hawaii)

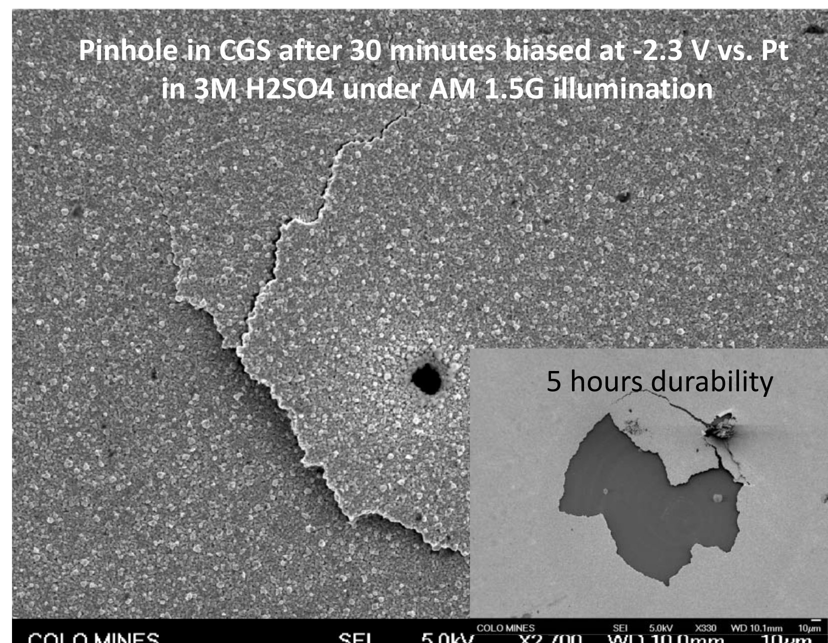
- CGS is a thin film semiconductor considered as the top junction in a tandem cell–must be durable
- Researched platinum catalysts treatments - Inconsistent results due to CGS variability

Figure 10-19: Type 3 Cost Sensitivities ($/kgH$_2$)



Hydrogen Cost ~$10/kg but PEC system benefits directly from PV cell cost reductions. Cost Reduction to ~$5.50/kg H$_2$ is quite possible.

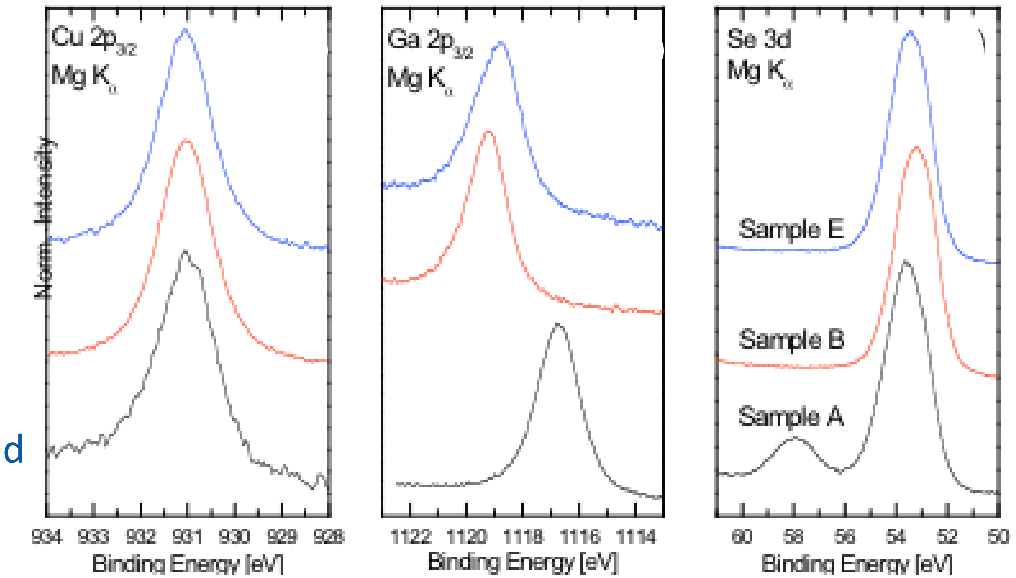
- Potentiostatic analysis for short duration (6-hours)
  - Mechanical instability
    - Pinholes/delamination
    - Could be due to fluorine doped tin oxide substrate
- Further analysis necessary to determine if it is chemically stable
  - XPS surface analysis
  - ICP-MS analysis of durability solutions



Technical Accomplishments and Progress

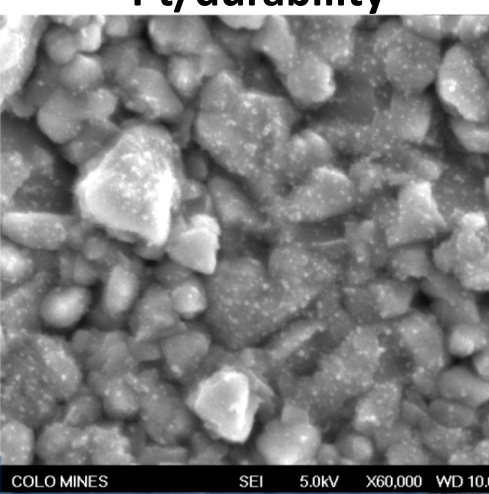
Chalcopyrite materials based on [Cu(In,Ga,Al)(S,Se,Te)$_2$]

- HNEI $CuGaSe_2$ baseline testing/UNLV XPS analysis
  - Biasing alters Ga environment
  - Electrolyte alters Se environment by removing SeO_2 (could be etching by acid)
- Durability testing with and without Pt catalyst
  - Evaluate corrosion by PEC performance and SEM imaging
  - So far insignificant differences

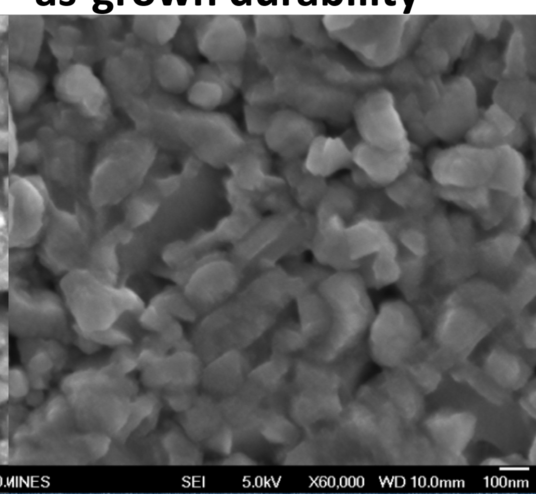


XPS showing Cu 2p, Ga 2p, Se 3d for $CuGaSe_2$ for (A) as grown, (B) tested w/o light, (E) tested w/ light

Pt/durability



as-grown durability

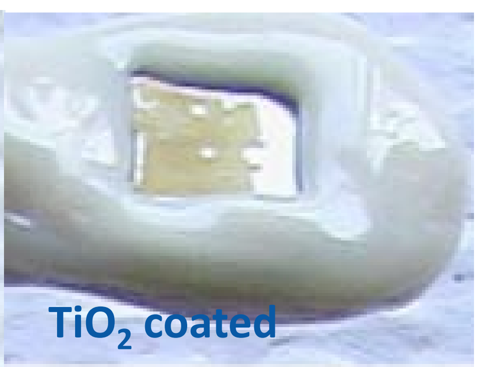


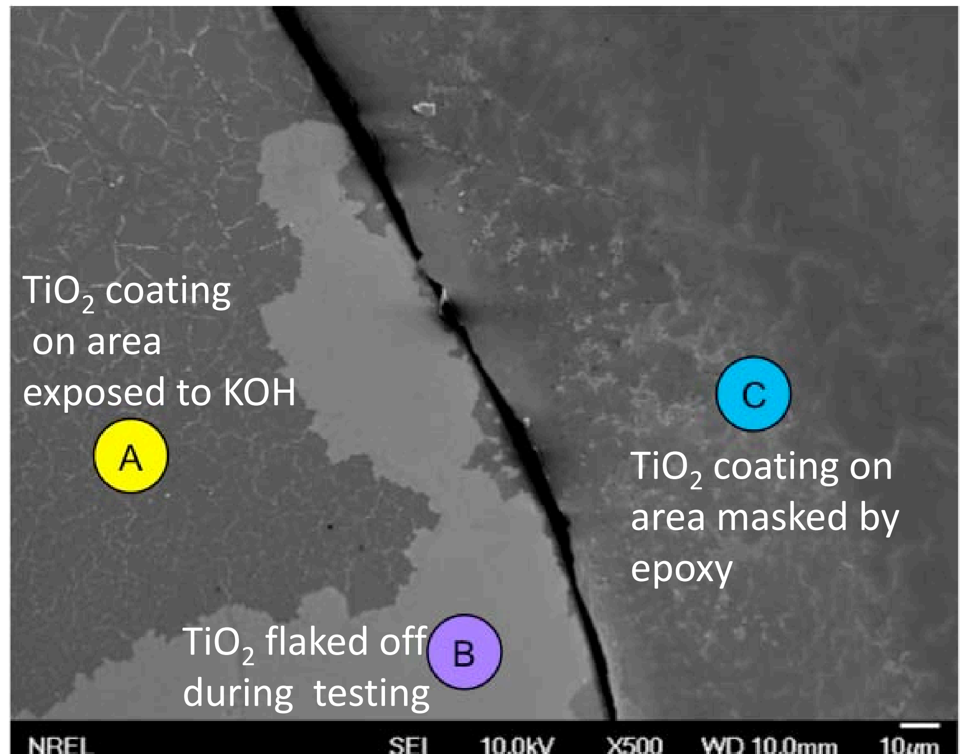
Technical Accomplishments and Progress

Protection Strategies for High-Efficiency III-V Photoelectrodes

- Coatings
  - ALD TiO_2, 20nm on p-$GaInP_2$
  - Portions of coating flaked off
  - Conditions not harsh enough to observe statistically significant protection
    - 22hrs, $5mA/cm^2$, 1M KOH
- Electrochemical nitridation
  - Preliminary results indicated surface was protected when run in NH_4NO_3
  - XPS found NH_3
  - Cation, Anion, Acid strength?

- $GaInP_2$/GaAs Tandem Cells
  - 12.4% Solar to hydrogen efficiency
  - Individual electrode performance is wafer-position dependent

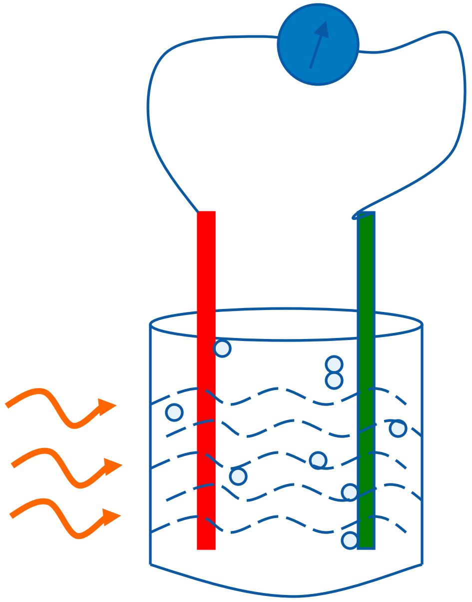




Approach for Oxide PEC Materials Search

Theoretical Screening of Oxides for Photoelectrochemical Hydrogen Production

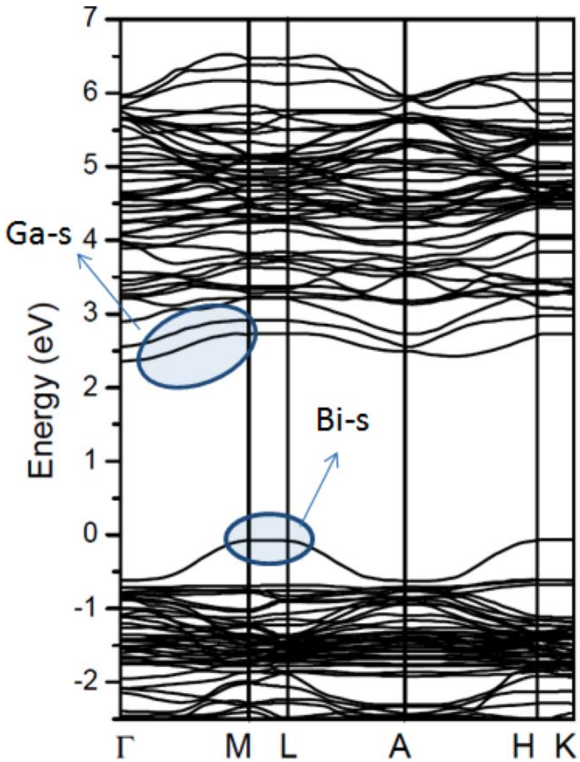
- Use theory to predict electronic (band) structures of unexplored materials
  - Calculate band gap and spectra
  - Calculate carrier mobility and band edge position (wrt vacuum)
- Synthesize promising materials
- Characterize
- Iterate with theory group

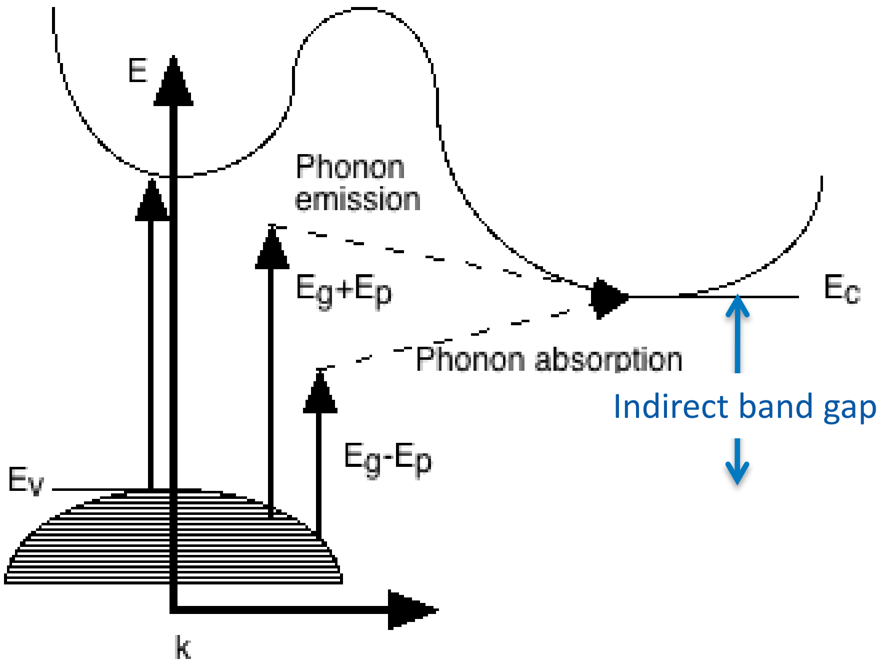


Technical Accomplishments and Progress

Theory of metal oxide, nitrides and other materials

- DFT calculations of Bi & Ga alloying of delafossites ($CuYO_2$)
  - Leads to reduced band gap
  - Reduced hole effective mass
  - Still an indirect transition



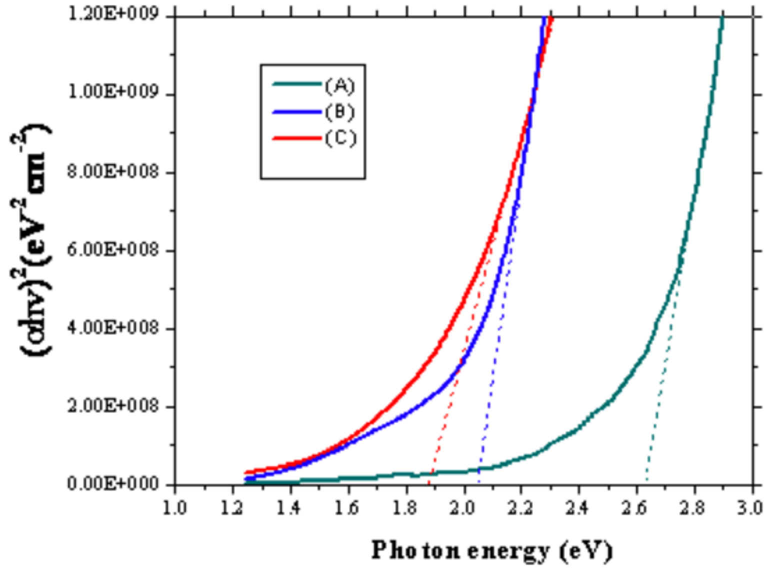


- Direct (vertical in band diagram) transition is preferred because it is more efficient, requires less material
- Degree of band curvature directly relates to carrier effective mass (mobility) and a flat band structure indicates poor mobility and likely a poor material

Technical Accomplishments and Progress

NREL synthesis of metal oxide alloy thin films

- Synthesis of Cu-W-O amorphous oxide materials by RF sputtering
  - Successfully reduced optical band gap
  - XRD indicates amorphous
  - Materials were unstable as PEC electrodes at high and low pH and non-responsive at moderate pHs
  - Explaination
    - WO_3 unstable in basic
    - CuO_2 unstable in acidic
  - May be possible to stabilize at neutral pHs using Co catalyst.
  - Currents were only a few microamps
  - No-go on further studies unless higher current system reported (watch list)



UV-Vis for (A) WO_3, (B) and (C) $CuWO_x$ with increasing Cu content

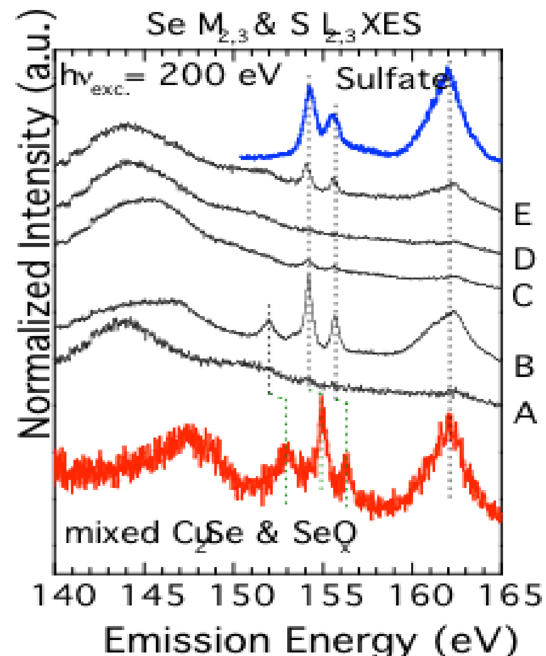
Technical Accomplishments and Progress

Advanced Characterizations

- Clemens Heske's group (UNLV)
  - UNLV Spectroscopic Analysis
  - Berkeley's Advanced Light Source Spectroscopies
- Determine semiconductor/catalyst interaction, corrosion mechanisms
  - Extend our understanding of these phenomena to an atomic level
- CGS, a-SiC, WO_3 analysis thus far
- III-V-N materials soon
- Details presented at Monday's poster session: PD051_Heske

Name in report	Sample Identification	Test parameters
A	CGS 090202-13 4	control
B	CGS 5	In 0.5M H_2SO_4 for 24 hr in dark
C	CGS 090202-22 1	Illuminated OCP, 0.5M H_2SO_4, 2 fiber optic illuminators, 60 s: 20 dark, 20 light, 20 dark
D	CGS 090202-22 2	3E Chopped light IV, 0.5M H_2SO_4, AM1.5,-1.0 V vs. Ref to 0.05 vs. open circuit, chop every 100 mV
E	CGS 090202-13 3	Illuminated OCP, 2E: -2.5 V to 0.05, 3E IV: -1 V to 0.05 V, performed in this order

X-ray Emission Spectra from CGS samples sent to UNLV



Technical Accomplishments and Progress

PEC Standards group

- Literature on PEC material characterizations does not adhere to "accepted" methods and standards
- Multiple year project on developing and publishing methods and standards for reporting (efficiency defined)
  - Contributors from NREL, DOE, Stanford University, University of Hawaii, UC Santa Barbara, University of Louisville, University of Tokyo and Australian Nuclear Science and Technology Organization International
  - **Huyen Dinh (NREL) facilitated**
- Published abbreviated Review paper in Journal of Materials Research
  - January 2010
- Currently seeking feedback from broader community on sharepoint site
  - National and International reviewers
  - Goal is to incorporate reviewers' suggestions, modify documents, and publish
- Considering venue for publication of lengthy report in a technical report or book.

http://www2.eere.energy.gov/hydrogenandfuelcells/pec_standards_review.html

Collaborations

Partners (extensive collaboration with all)

- University of Nevada Las Vegas
  - Samples sent to Heske group for X-ray spectroscopic characterization (ALS)
- Colorado School of Mines
  - Graduate and undergraduate research associates, electron microscopy
- University of Colorado
  - Undergraduate research associates
- University of Hawaii
  - CGS and RuO_2 from Hawaii for Pt catalyst studies; cooperative PEC characterization
- Stanford University
  - Jaramillo group- collaboration on nanostructured transition metal dichalcogenides
- University of Louisville
  - Sunkara group- ALD of TiO_2 on $GaInP_2$
- Los Alamos National Lab
  - Todd Williamson synthesizes InGaN samples
- Small Business Innovation Research
  - Synkera Technologies, Inc. (Industry)
    - Characterization of novel electrode structures and materials
  - Physical Optics Corp. (Industry)
    - Logistical support and consulting
- Program production solicitation
  - MVSystems, Inc. (Industry)
    - Characterization and durability analysis of a-SiC:H & a-SiN:H on materials provided by MVSystems

Proposed Future Work

- Investigate MBE grown p-InGaN and conductive substrates
  - p-type for cathodic protection
  - Conductive substrates for improved efficiency
- Further UNLV analysis & discussions to understand how spectroscopy results correlate with PEC test parameters
- Investigate protective coatings and treatments for proven high-efficiency materials that suffer from instability
  - Thin coatings by ALD
  - Electrochemical nitridation
  - Plasma nitridation
  - Ion bombardment nitridation
- Explore other substrates for CGS durability
  - Ultimate application is tandem cell
  - Si more realistic substrate
- Synthesis and characterization of oxide materials
  - Cu-Ti-O system
  - $CuGaO_2$ delafossites
- Investigate alternative oxygen evolution catalysts as counter electrodes to improve photocathode efficiency
  - RuO_2, IrO_2, Co (phosphate)

Summary

- Identified possible contact strategy capable of improving InGaN water splitting efficiency that could satisfy technical target (10%)
- We down-selected a-SiN and Cu-W-O materials that demonstrated poor performance and stability
- We determined the efficiency and stability of a-SiC/a-Si hybrid photoelectrodes
  - Low efficiency-compared with solid-state
  - Durability must be improved to meet 1000-hour technical target
- Led the effort to establish standardized measurement and reporting practices for PEC materials

Summary

- A viable PEC water splitting system requires a unique material that satisfies several specific requirements
  - No known material is suitable
  - Incremental progress has been made enhancing stability and efficiency
- New materials must be synthesized and characterized
  - Guided by rational theory, synthesis, characterization feedback
  - Not going to meet DOE technical targets with slight modifications of the usual (oxide) suspects
- Primary focus is finding a suitable material; secondary concern is developing a high-throughput/low-cost synthesis route

Acknowledgements

- Kim See - Colorado School of Mines
  - CGS, SEM
- Jane Henderson- University of Colorado, Boulder
  - SiN, SEM
- Josh Morton - University of Colorado, Boulder
  - SiC
- Alexandra Chakeres- Washington University, St. Louis
  - InGaN
- Leah Kuritzky - Stanford University
  - InGaN
- Ryan Jones- Emory University
  - SiN
- Heli Wang - NREL
  - $GaInP_2$ nitridation
- Ashley Gaulding, University of Minnesota
  - TiO_2 coated $GaInP_2$, SEM