National Renewable Energy Laboratory
Innovation for Our Energy Future

Semiconductor Materials for Photoelectrolysis

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Overview

Timeline

- Project start date: 1991
- Project end date: 2018
- Percent complete: n/a

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: $8.0M
- Funding received in FY08: $2235k
- Funding for FY09: $1385k

Partners

Interactions/ collaborations

- University of Nevada Las Vegas
- Colorado School of Mines
- University of Colorado
- University of Hawaii
- Stanford University
- Program production solicitation
  - MVSystems, Inc.

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]

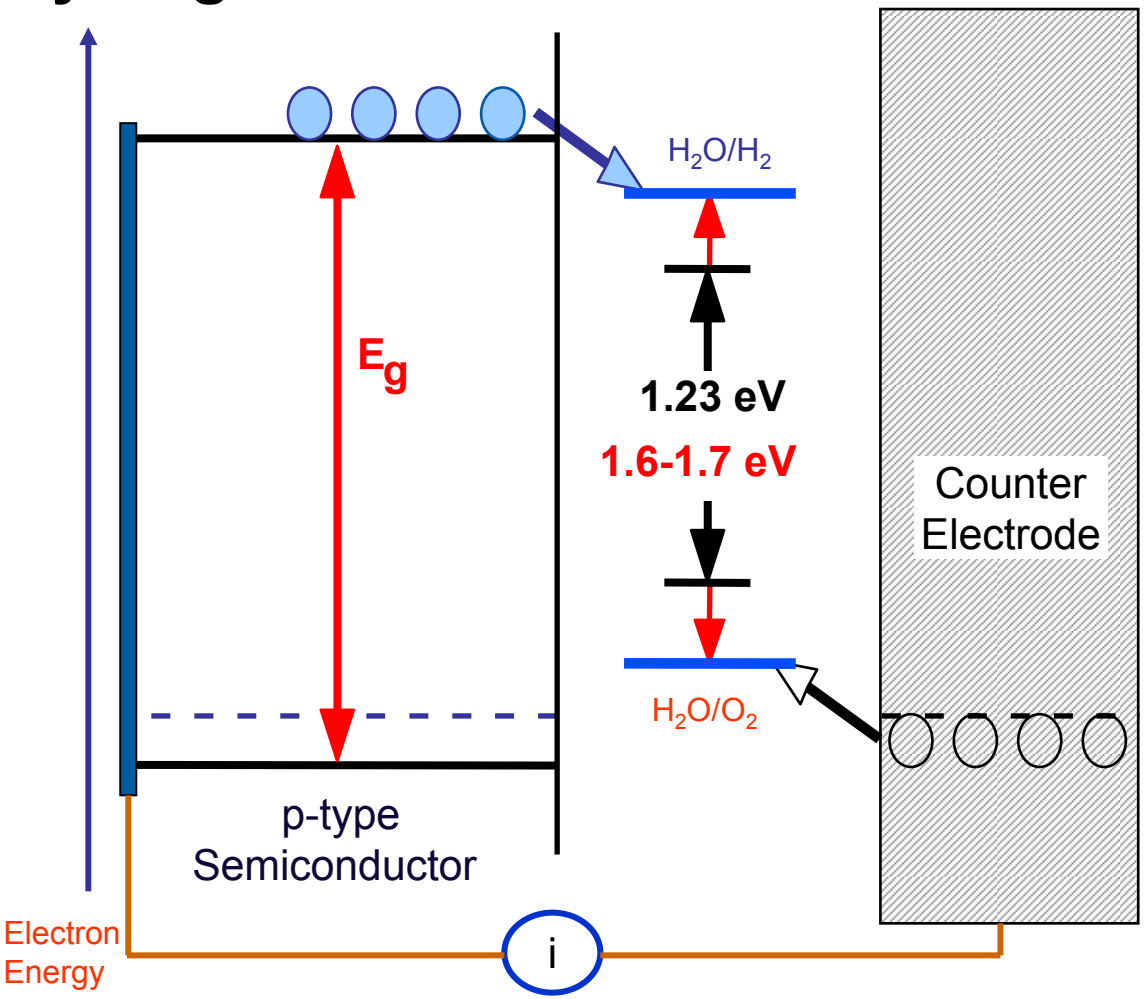
Characteristics	Units	2003 Status	2006 Status	2013 Target	2018 Target [b]
Usable semiconductor bandgap [c]	eV	2.8	2.8	2.3	2.0
Chemical conversion process efficiency (EC) [d]	%	4	4	10	12
Plant solar-to-hydrogen efficiency (STH) [e]	%	not available	not available	8	10
Plant durability [f]	hr	not available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

Milestones/Relevance

	Milestone	Completion Date
3.4.1	Complete experiments on the water-splitting efficiency of a system based on InGaN 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
3.4.3	Complete study of corrosion testing to estimate stability of improved single-phase CIGSSe material for application to a tandem cell	03/09
3.4.6	Complete evaluation of Co-Fe-Al oxide and go/no-go for additional studies	12/08

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 simultaneously.

Approach

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

Non-Oxides

III-V materials have the highest solar conversion efficiency of any semiconductor material

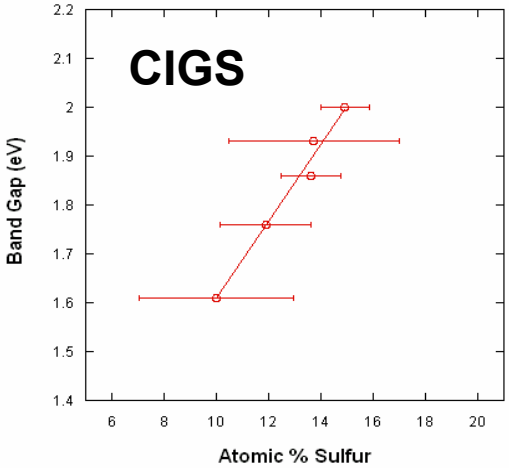
- Large range of available band gaps (0.7eV – 3.4 eV)
  - Stability an issue – nitrides show promise for increased lifetime (Barriers Y & Z)
  - Band-edge mismatch with known materials – tandems an answer (Barrier AC)

I-III-VI materials offer high photon conversion efficiency and possible low-cost manufacturing

- Synthesis procedures for desired band gap unknown (Barrier AB)

Other thin-film materials with good characteristics

- SiC: low-cost synthesis, stability (Barrier AB)
- SiN: emerging material (Barrier AB)



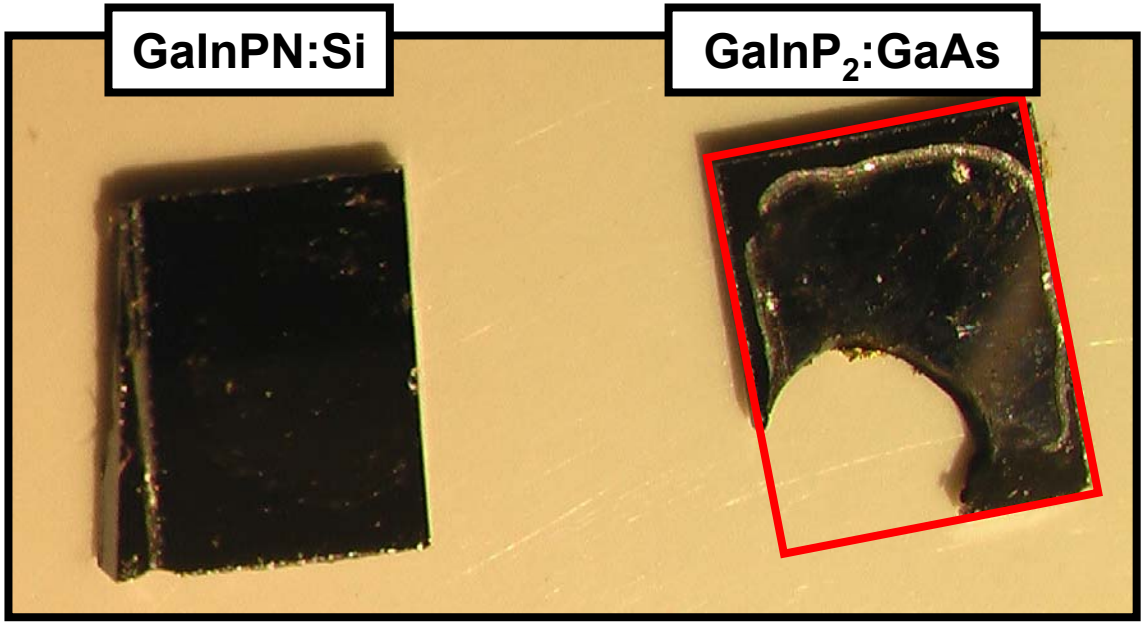
Mixed Metal Oxides

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

Technical Accomplishments and Progress

In addressing the MYPP barriers Y and Z, using indium as a lattice expander, we were able to achieve higher amounts of nitrogen in our III-V tandem materials. Corrosion testing of GaInPN material showed the capability of reaching the DOE MYPP 2013 target of 1000 hrs of operation however, the solar conversion efficiency was low, about 1%. In light of the promising results, more work on these materials is warranted.

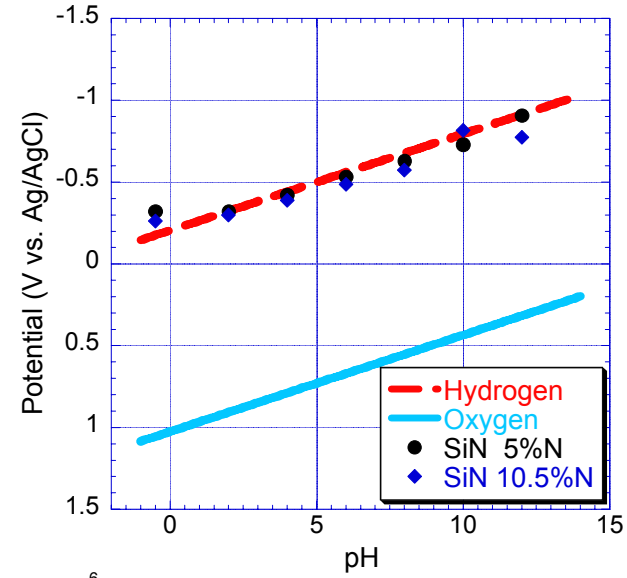
- $Ga_{.95}In_{.05}N_{.025}P_{.975}$ lattice-matched to silicon
- 24-hour corrosion test
  - Constant 5 mA/cm^2 applied current
  - Sample illuminated at 1 sun
- Profilometry etch depth
  - ~ 0.1 µm for GaInPN
  - ~ 1 µm for $GaInP_2$



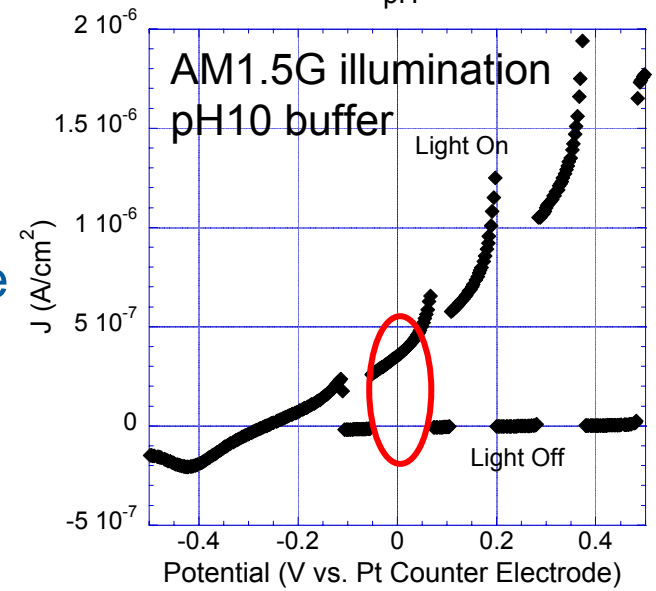
Technical Accomplishments and Progress

In addressing the MYPP barriers AB and AC, our efforts on SiN have realized a material that has appropriate band edge positions for water splitting and has a band gap of less than 2.0eV, in the region for efficient photoconversion. This meets the 2018 DOE target for band gap, but does not yet meet the efficiency target. Because of the favorable band edge positions, band gap, and stability, research on SiN will continue.

- Conduction band edge positions for n-SiN from Illuminated OCP measurements
- Appropriate for water splitting

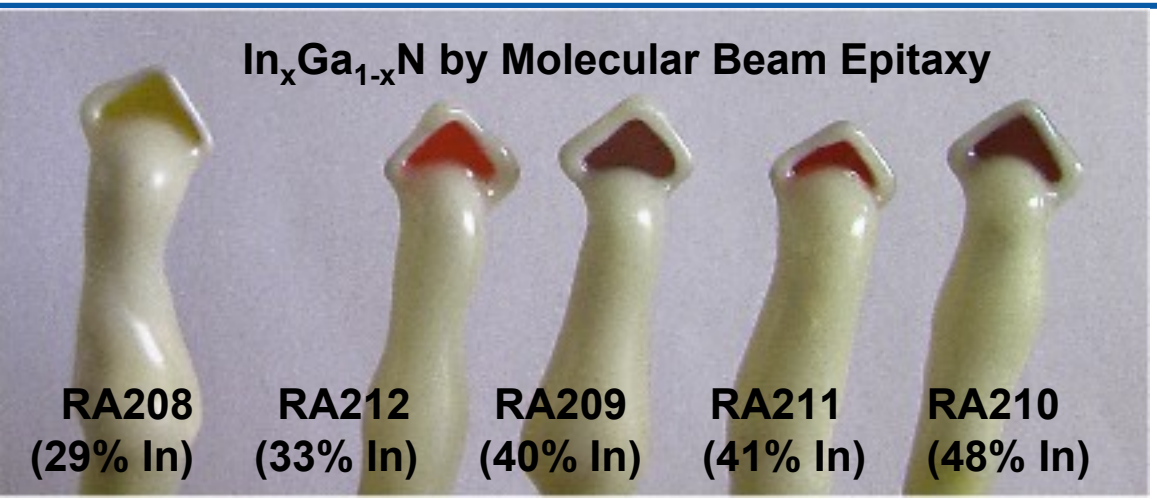


- Photocurrent at zero applied bias (red oval) indicate unbiased PEC water splitting



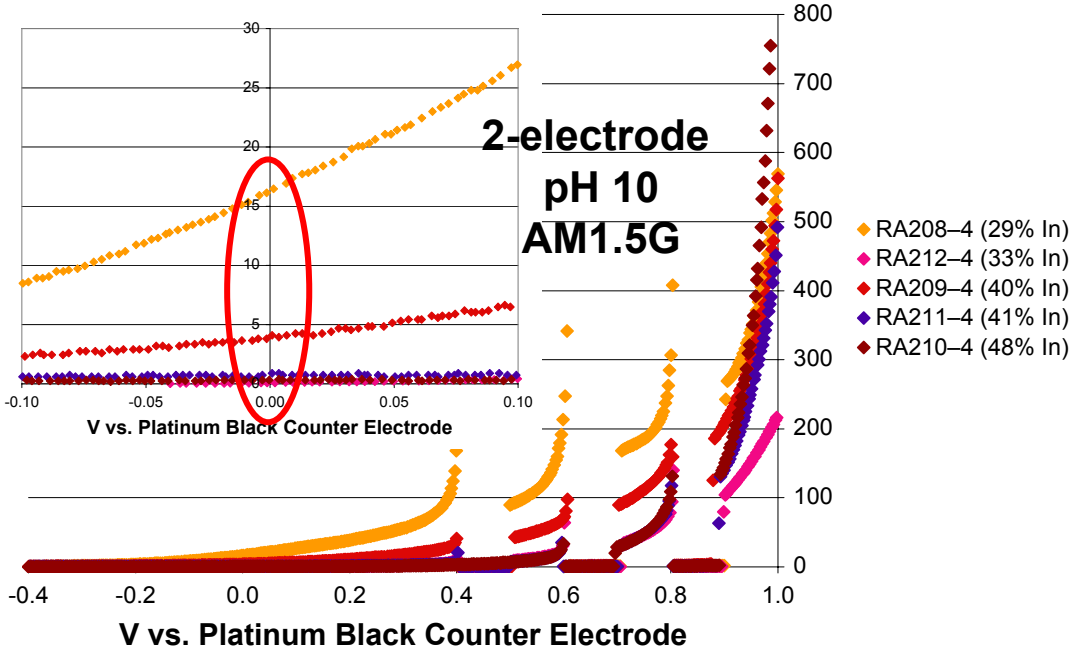
Hot Wire Chemical Vapor Deposition

Technical Accomplishments and Progress



- Tunable band gap in visible region
- Band edge alignment
  - M-S: aligned
  - OCP, PConset: mismatched
- Unbiased water splitting
- Durability not assessed yet

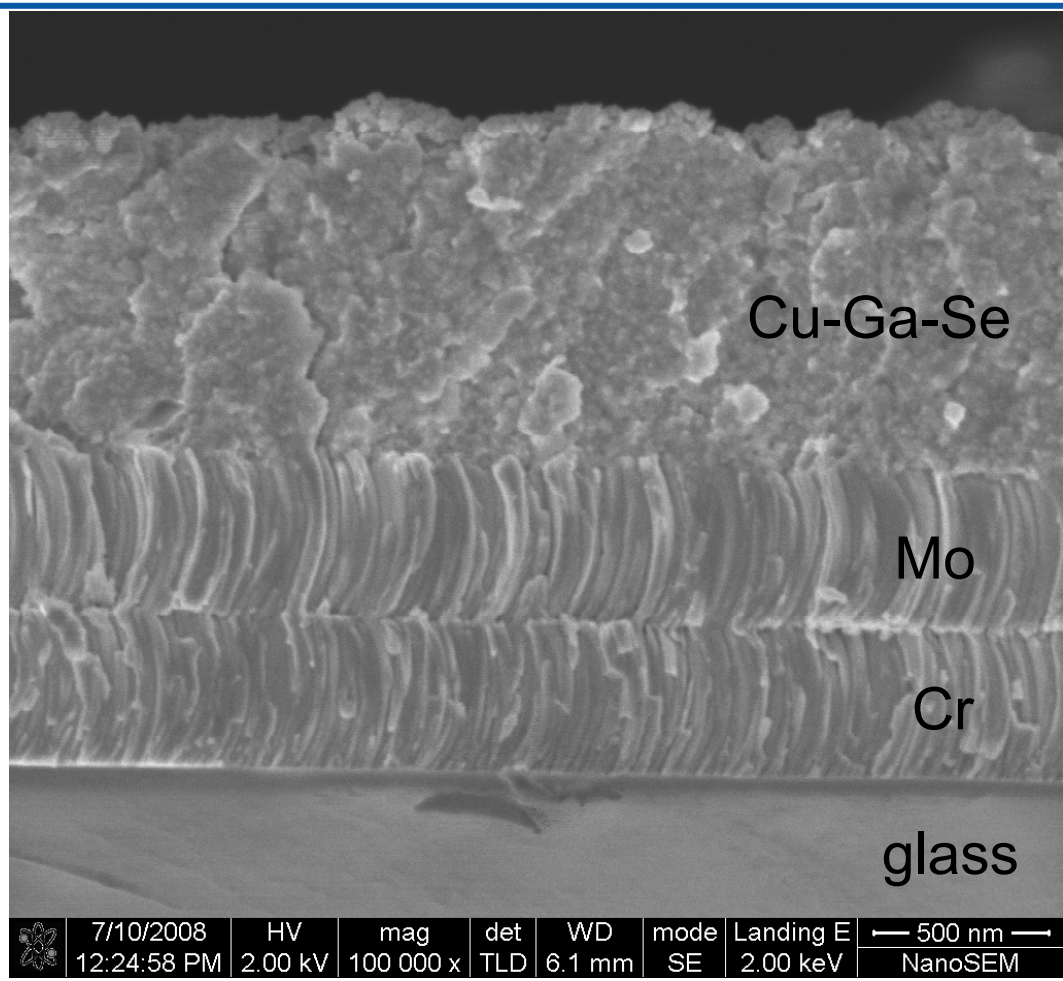
Our efforts on InGaN have realized a material that has appropriate band edge positions for water splitting and, for most compositions, has a band gap of less than 2.0eV, in the region for efficient photoconversion. This meets the 2018 DOE target for band gap, but does not yet meet the efficiency target. Studies are planned on additional alloy compositions and synthesis techniques.



Technical Accomplishments and Progress

Electrodeposition of Chalcogenides

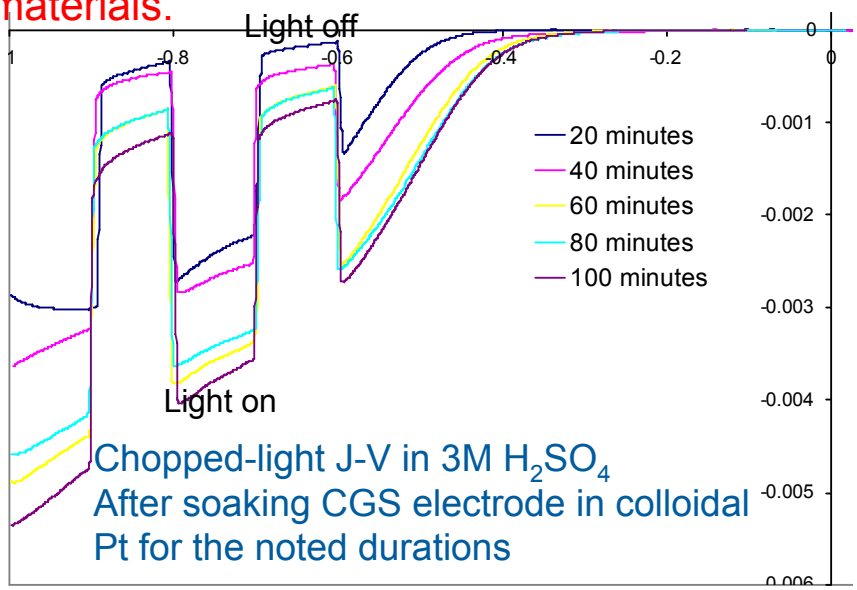
In addressing the MYPP Y and AB challenges, we have further refined the electrodeposition synthesis conditions to optimize the quality and repeatability of electrodeposited copper gallium selenide (CGS) thin films. Very good quality films with high reflectivity and uniformity across the surface and good adhesion to the substrate can now be made reproducibility. We anticipate that once annealed, these films will be able to meet the 2018 DOE target for band gap. Research will continue on to optimize this inexpensive synthesis route.



The Cu-Ga-Se layer depicted above was synthesized from an electrolytic bath made with 1.36 mM of $Cu(NO_3)_2$, 10 mM of $Ga(NO_3)_3$, 8 mM of H_2SeO_3, and 1 M of $LiNO_3$. The applied potential was -0.6V vs Pt, over 30 min at room temperature.

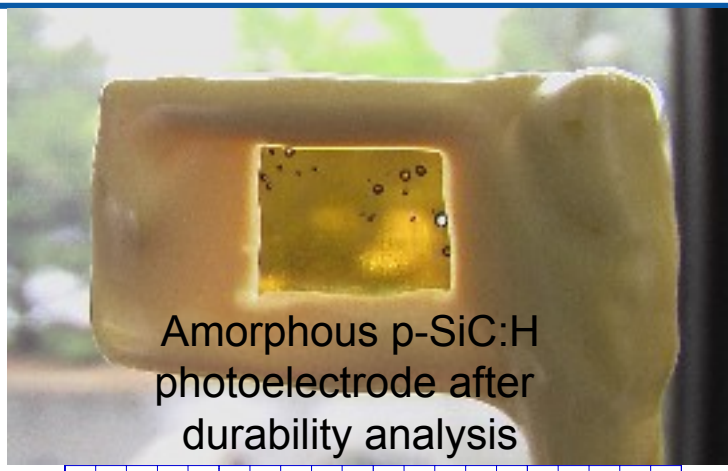
Technical Accomplishments and Progress

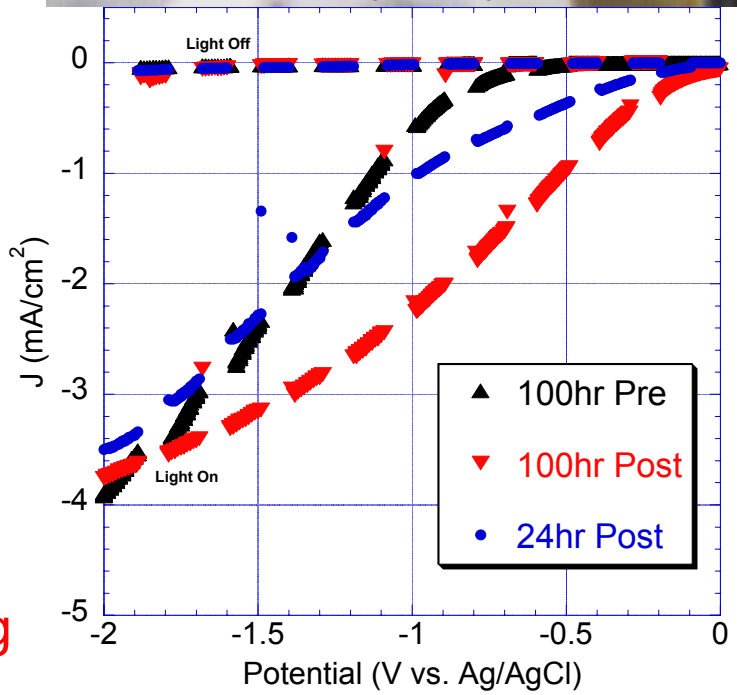
We initiated studies on platinum surface catalyst optimization for maximizing cathodic photocurrent on p-type $GaInP_2$, Ga(In)PN, and (in collaboration with the University of Hawaii) CGS electrodes. The two techniques we are studying are electrodeposition from chloroplatinic acid and adsorption of Pt colloids from neutral solutions. Platinum has been observed on electrode surfaces by SEM and the chemical signature detected by EDS. Pt increased the magnitude of photocurrent and shifted the onset to lower potentials indicating catalysis. We plan to adapt the catalyst treatment for other materials.



Technical Accomplishments and Progress

In collaboration with MVSystems, Inc. we performed durability analysis on p-SiC:H photoelectrodes. These materials are made by Plasma Enhanced Chemical Vapor Deposition (PECVD), a process that can be high-throughput and has demonstrated commercial success for PV materials. We tested this durable material as a stand alone absorber and as a protective coating for tandem cells. This material addresses several MYPP barriers (Y, Materials Efficiency; Z, Materials Durability; AB, Bulk Materials Synthesis; AC, Device Configuration Designs)





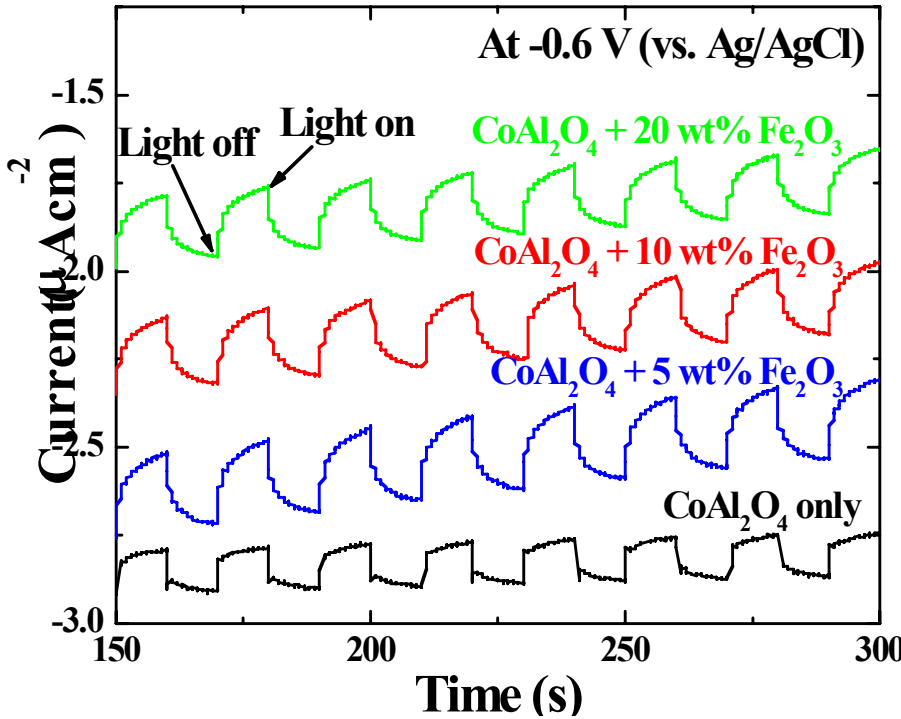
Chopped Light J-V in pH 2 Buffer
As grown (100hr Pre)
After 24 hours durability testing (24hr Post)
After 100 hours durability testing (100hr Post)

Durability testing: -3mA/cm^2, pH2, AM1.5G

Test results indicate stable material
Electrode remained viable after extended testing
Research on this material will continue

Technical Accomplishments and Progress

Nanocrystalline composite Co-Fe-Al oxide electrodes, were synthesized by DC magnetron sputtering. Though these novel materials demonstrated a p-type response to illumination, an exciting result for oxide-based electrode materials, they yielded a very low photoresponse. NREL's theory group developed a breakthrough thesis that shed light on why this material as well as a whole family of oxides will never work; because they belong to a category of materials known as Mott insulators. In light of the theory and continued poor experimental performance, we decided further study of this material class is a **no-go**.



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 from Hawaii for Pt catalyst studies; cooperative PEC characterization
- Stanford University
  - Collaboration initiated on nanostructured transition metal dichalcogenides
- Program production solicitation
  - MVSystems, Inc. (Industry)
    - Characterization and durability analysis of a-SiC:H & a-SiN:H materials provided by MVSystems

Proposed Future Work

Non-Oxides

- InGaN samples by other techniques
  - Laser-assisted MBE (LANL), MOCVD(Texas Tech)
- a-SiN:H by alternate deposition method
  - PECVD (MVSystems)
- Optimize Pt hydrogen catalyst for all photocathodes
- Isolate and optimize oxygen catalyst for photoanodes
- Investigate atomic layer deposited protective coatings (University of Louisville)
- Electrodeposition of nitride semiconductors

Oxides

- Additional promising mixed metal oxides

- Continue to support other members of the PEC working group

Summary

- We downselected an oxide material (CoFeAlO) that has insurmountable intrinsic shortcomings (it is a Mott insulator)
- Isolated two materials that appear to have appropriate interfacial energetics to split water without applied bias (InGaN and SiN)
- Confirmed stability of nitride and carbide materials
- Improved efficiency through catalyst treatments
- Led a diverse team tasked with establishing standardized procedures for photoelectrochemically characterizing semiconductor samples for water splitting (to be published soon)

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
- Joseph Ryerson - University of Colorado, Boulder
  - SiN, SEM
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  - SiC
- Sally Pusede - University of California, Berkeley
  - InGaN
- Arturo Fernandez - UNAM (Mexico)
  - CGS electrodeposition
- Heli Wang - NREL
  - $CoAlFeO_x$
- Leah Kuritzky - Stanford University
  - SiN