NREL
NATIONAL RENEWABLE ENERGY LABORATORY

Semiconductor Materials for Photoelectrolysis

DOE Hydrogen Program
Annual Merit Review

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Project ID: PD035

May 12, 2011

Overview

Timeline

- Project start date: 1991
- Project end date: 10/2011*
- Percent complete: 98%

Budget

- Total project funding
  - DOE share: $11M
- Funding received in FY10: $1100k**
- Funding for FY11: $1100k**

* Project continuation and direction determined annually by DOE

** Includes UNLV and SU support

Barriers

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

Partners

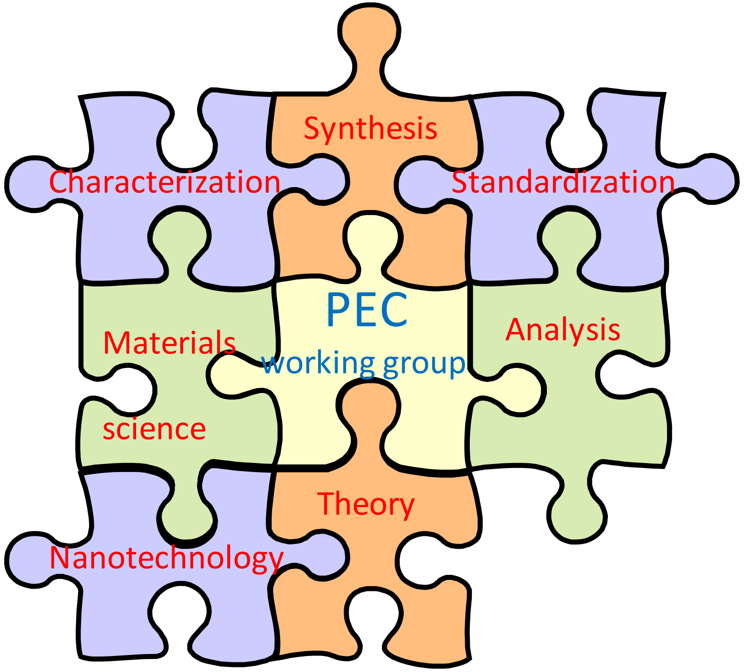
- Interactions/collaborations
  - Los Alamos National Laboratory
  - Lawrence Livermore National Lab
  - University of Nevada Las Vegas (UNLV)
  - Colorado School of Mines
  - University of Louisville
  - University of Hawaii
  - Stanford University (SU)
  - Program production solicitation
    - MVSystems, 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 high 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



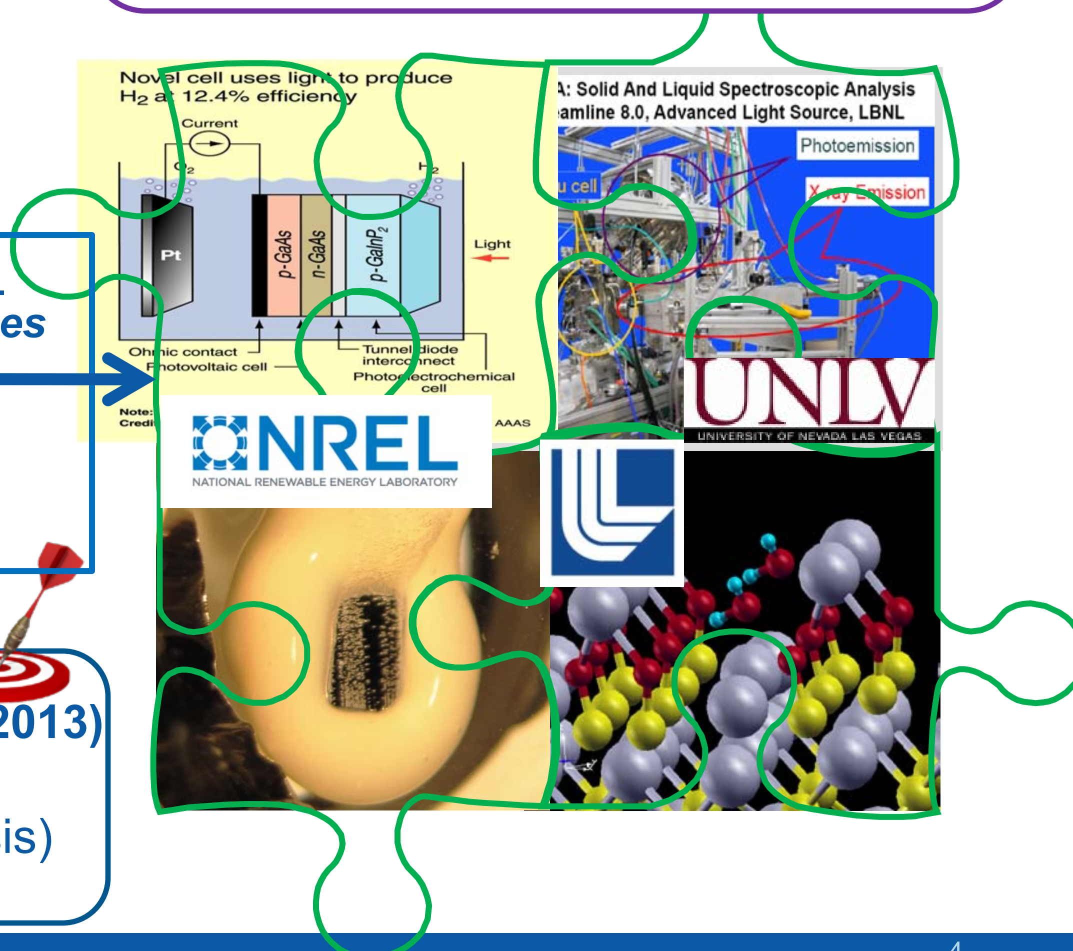
Relevance/Approach

PEC Working Group:
Review and evaluate technical progress
Initiate and foster collaborations
Leverage shared knowledge to accelerate progression towards overall goal

NREL Assumes Primary Leadership in:
- ***High Efficiency III-V Materials & Devices***
- ***III-V Surface Validation Study***

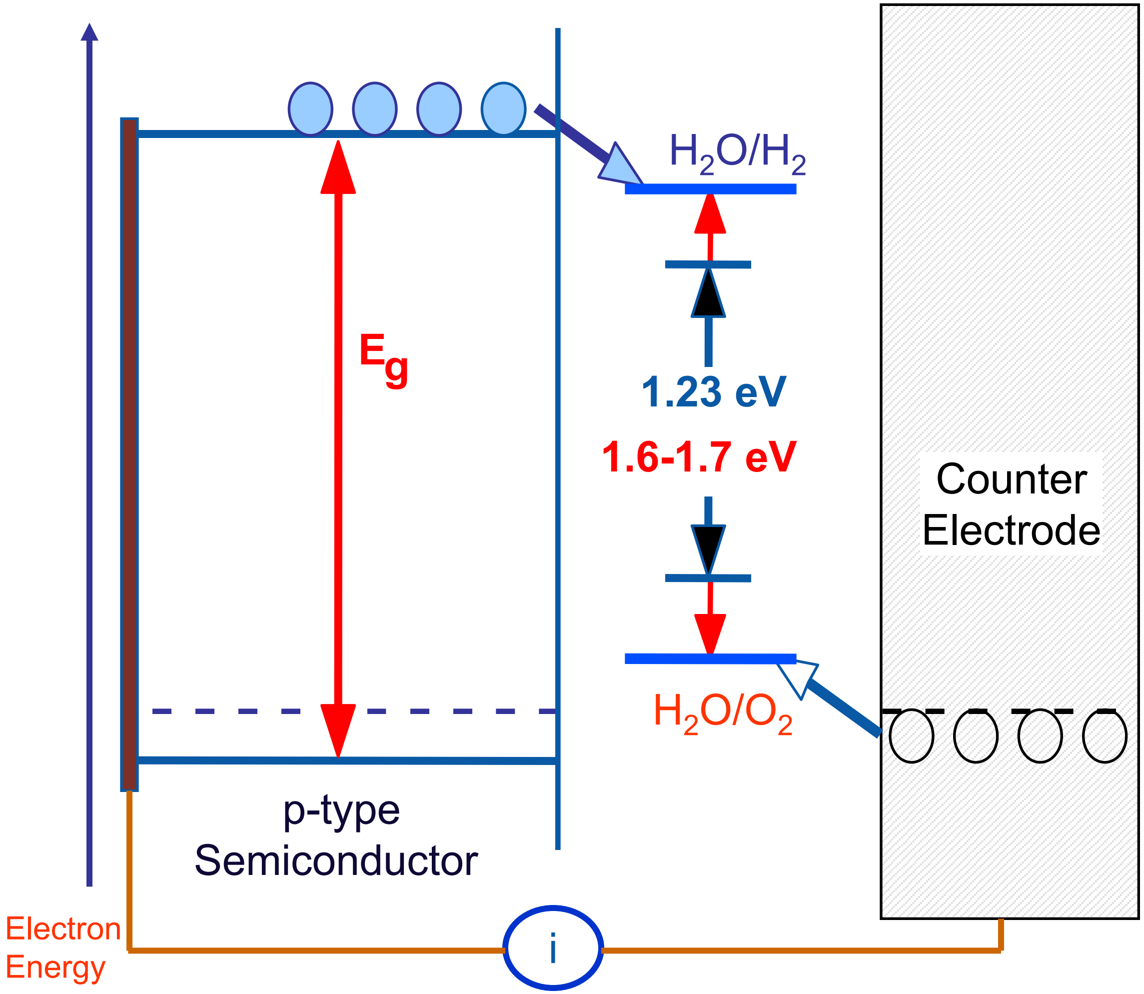
Important Supporting Role in :
- ***Thin-Film Materials Development***
- ***Nano-particle Catalyst Materials***

DOE Targets: >1000h @STH > 8% (2013)
\$2 - 4/kg H_2 projected PEC cost
(beating >\$10/kg H_2 for PV-electrolysis)



Material Challenges *(the big three)*

Characteristics for an Ideal Photoelectrochemical Hydrogen Production Material



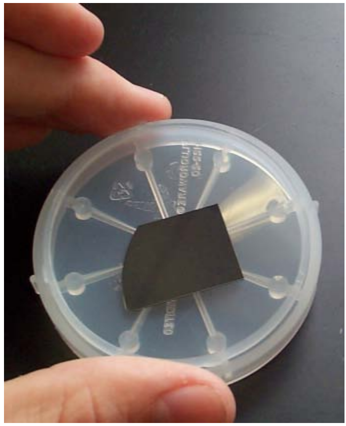
- **Efficiency –** band gap (E_g) must be at least 1.6-1.7 eV, but not over 2.2 eV; must have high photon to electron conversion efficiency
- **Material Durability –** semiconductor must be stable in aqueous solution
- **Energetics –** band edges must straddle H_2O redox potentials (Grand Challenge)

All must be satisfied simultaneously.

Approach: New Materials Discovery

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)

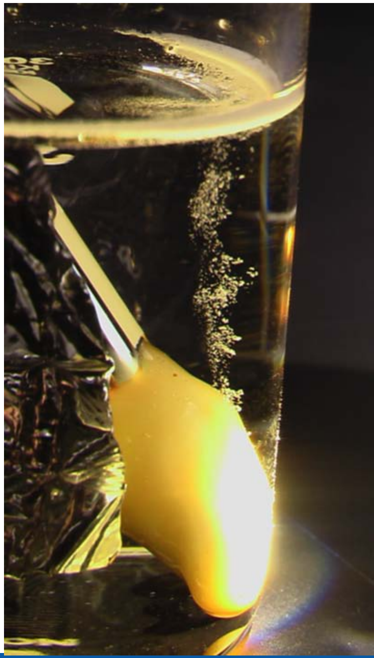
- Direct transition band gap, couple µm's of material, not 100's of µm
- Large range of available band gaps (0.7eV – 3.4 eV)
  - Stability an issue – nitrides show promise for increased lifetime (Barriers Y & Z)
  - Band-edge mismatch with known materials – tandems an answer (Barrier AC)

I-III-VI materials offer high photon conversion efficiency and possible low-cost manufacturing–$Cu(In,Ga,Al)(S,Se,Te)_2$

- 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)



Mixed Metal Oxides

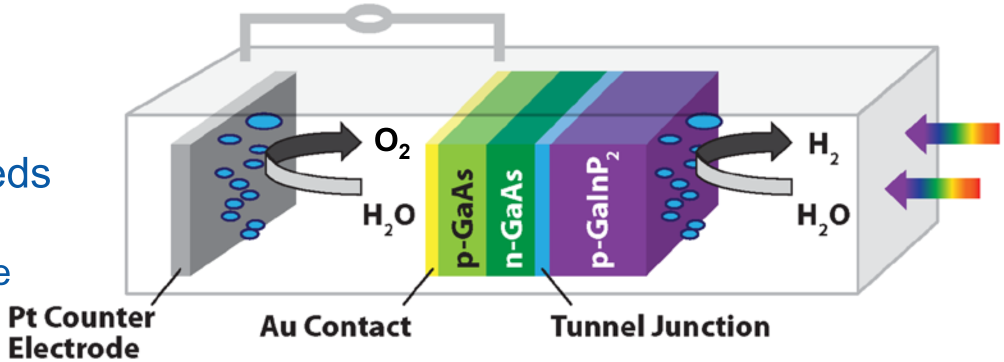
- Theory-Density Functional Theory (DFT) calculations to identity promising candidates
- Synthesis and characterization
- Cu, W, Bi, Sb based ternary or multinary oxides

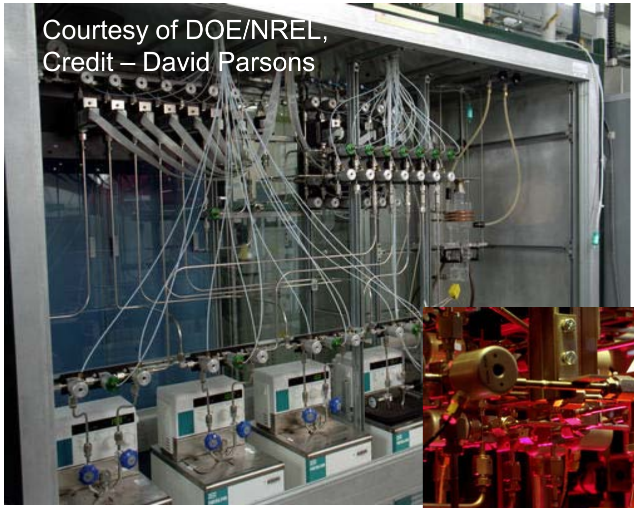
Approach: Engineering Known Materials

Enhancing durability of a high efficiency system through material engineering

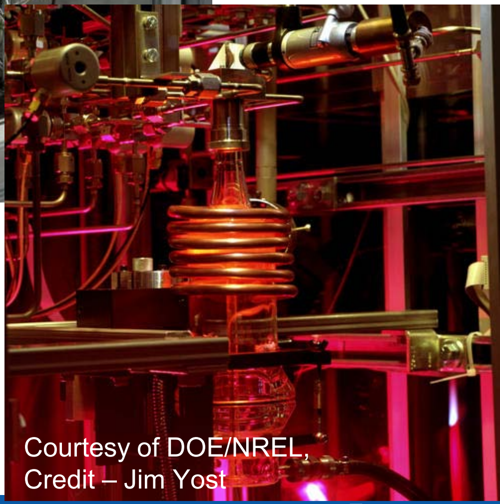
GaInP$_2$/GaAs tandem

- Metal Organic Chemical Vapor Deposition (MOCVD) synthesis
- Only demonstrated system that exceeds 10% solar-to-hydrogen target
  - 12.4% with Pt-black counter electrode
  - Greater efficiency with RuO$_2$ CE (Raising the bar!)
- Prone to corrosion
  - Unknown mechanism
  - Understanding pathway is nontrivial task
  - Fundamental need to identify and decipher corrosion in order to develop countermeasures
- Ideal candidate for corrosion studies
  - Single crystal surface
    - Easier to observe surface/changes
    - Easier to model and understand
  - Can tolerate efficiency losses due to protective treatment and still meet 10% target
- Dilute nitrides (1% N in GaPN, GaInPN) have improved stability in III-V PEC systems
  - Nitride in bulk lowers conversion efficiency
  - Nitride on surface offers protection





MOCVD reactor



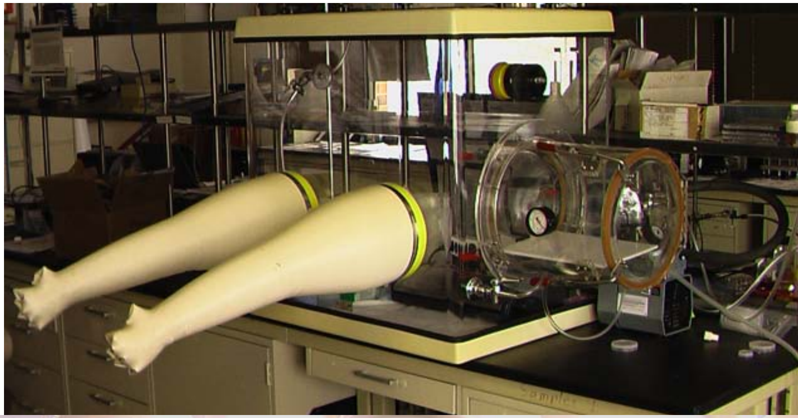
JPCB, 2006, **110**, p.25297.
JES, 2008, **155**:9, p.B903.

Approach: Engineering Known Materials

Partner with specialists with unique expertise and resources

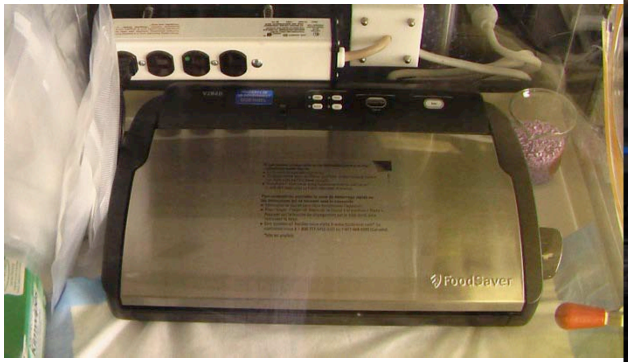
Surface Validation Team

- Partner with UNLV (Heske) (PD051)
  - XPS, XAS, XES, IPES, UPS, AFM
  - Snapshots of surface pre-, intermediate, post-exposure
  - Identify common features of and conditions that lead to corrosion
  - Future: XAS & XES in-situ?
- Partner with LLNL (Ogitsu) (PD058)
  - Molecular dynamics simulations
  - Model surfaces for mechanistic understanding of corrosion
  - Calculate XAS and XES spectra to correlate experimental result with surface/near surface compositions



Goals

1. Understand PEC corrosion in III-V's, simplest (model) system to understand
2. Use understanding of corrosion initiation sequence to develop solution
3. Apply lessons learned to other inexpensive systems (polycrystalline thin-film, amorphous)



Technical Accomplishments and Progress

Efficiency benchmarking

Simulated sunlight

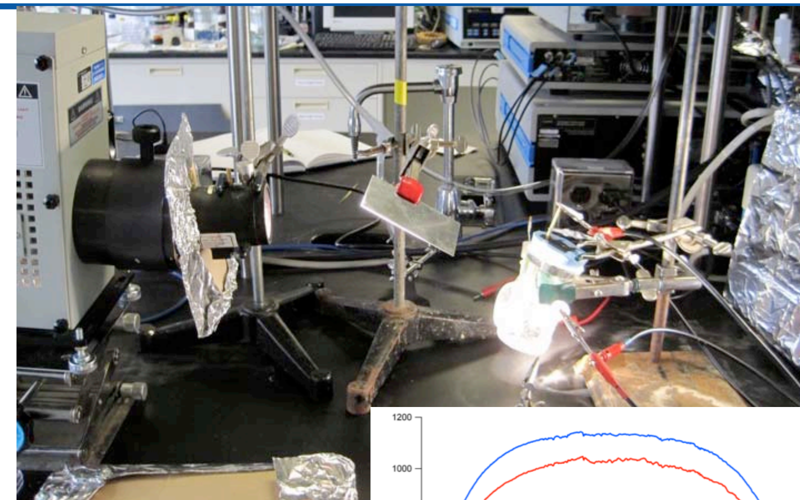
- Semiconductor (PV) reference cells calibrated to AM1.5 G
  - Different band gaps
  - Adjust lamp (tungsten, xenon) intensity until short-circuit matches calibrated value
  - Matches above E_g integrated intensity, not distribution
- Difficult to accurately simulate solar spectrum for multiple junctions

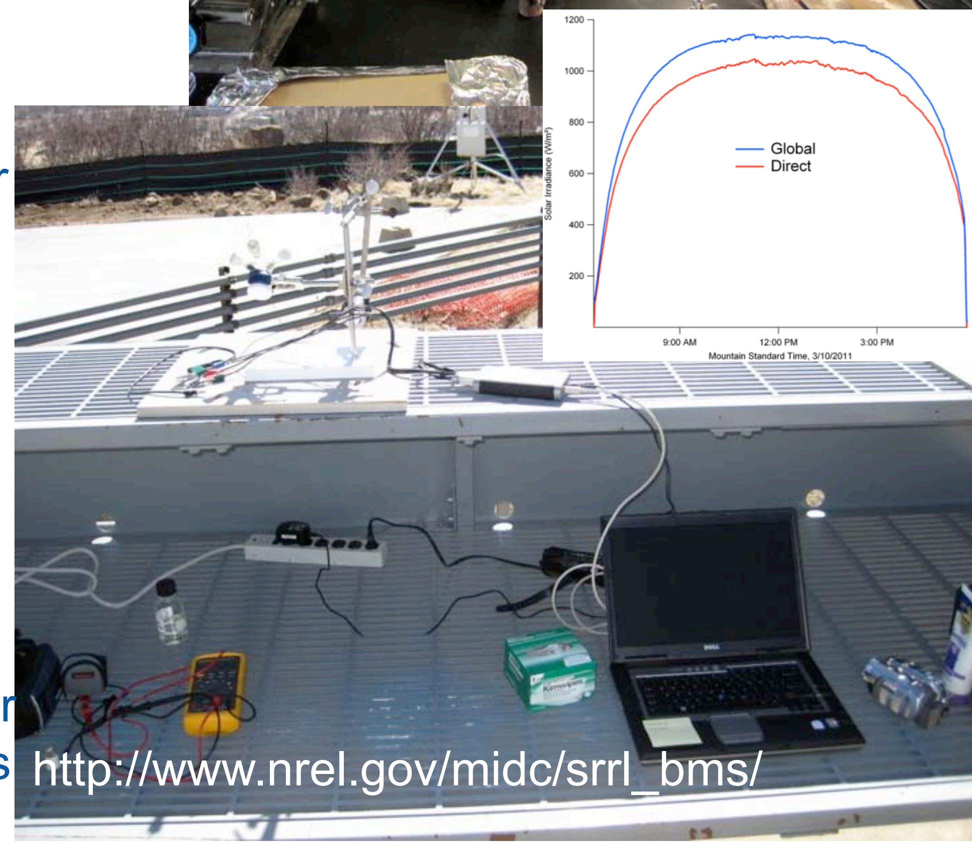
Outdoor measurements

- Solar Radiation Research Laboratory
  - 60-second interval direct, diffuse, global intensity
  - Spectral distribution

Gaseous product detection/analysis

- Developing gas chromatography for quantitative and qualitative analysis



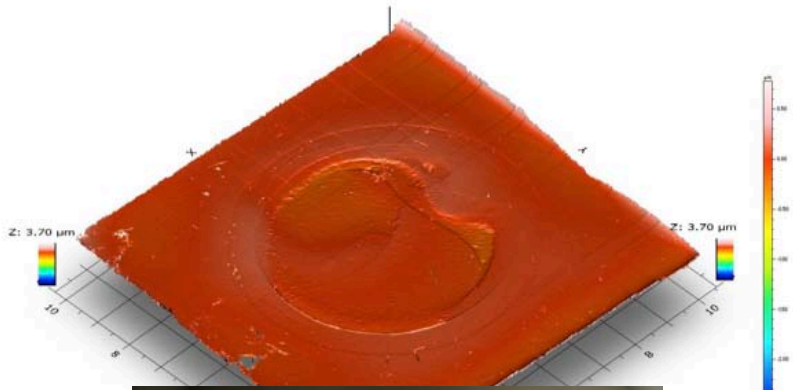


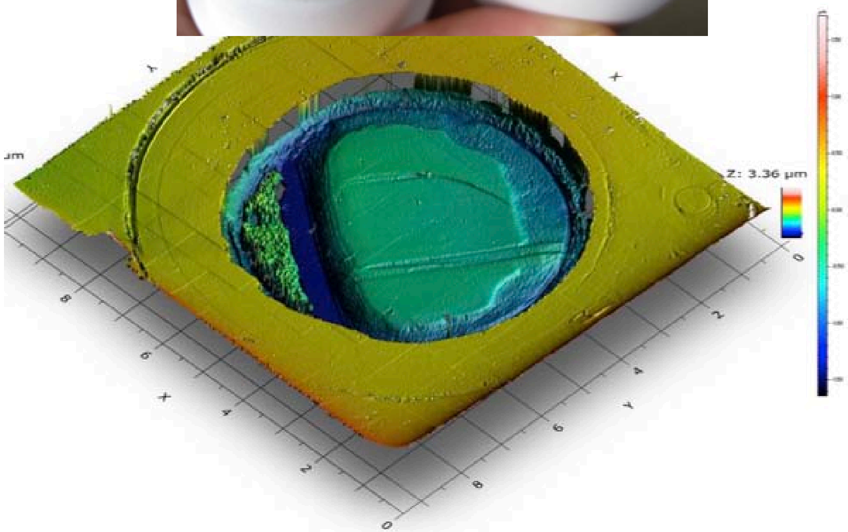
Technical Accomplishments and Progress

Durability benchmarking

Controlled static conditions

- Long-term continuous testing (indoor)
  - Stable lamp output
  - Galvanostatic or potentiostatic
    - Zero bias is ideal condition
  - 24, 100, 500 hrs
- Potential for outdoor real-world (variable) conditions
- Solution analysis by ICP-MS
  - Detect and quantify dissolved semiconductor components
- Sample post-mortem
  - Morphological characterization (interference scope, SEM, AFM)
  - Spectroscopic chemical characterization (XPS, IPES, AES, SIMS, XAS, XES)
    - NREL/UNLV
- In-situ spectroscopy (XAS, XES) with UNLV in nascent stages



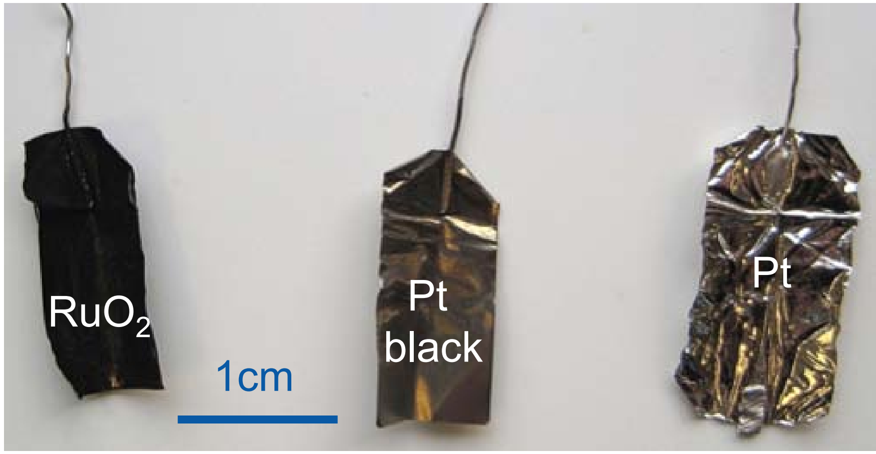


Technical Accomplishments and Progress

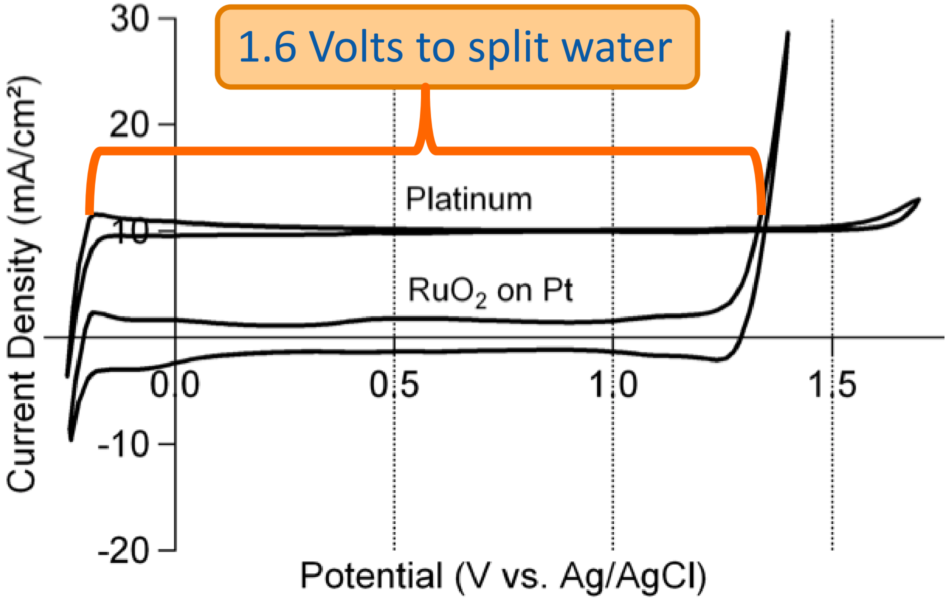
Improved efficiency of standard bearer

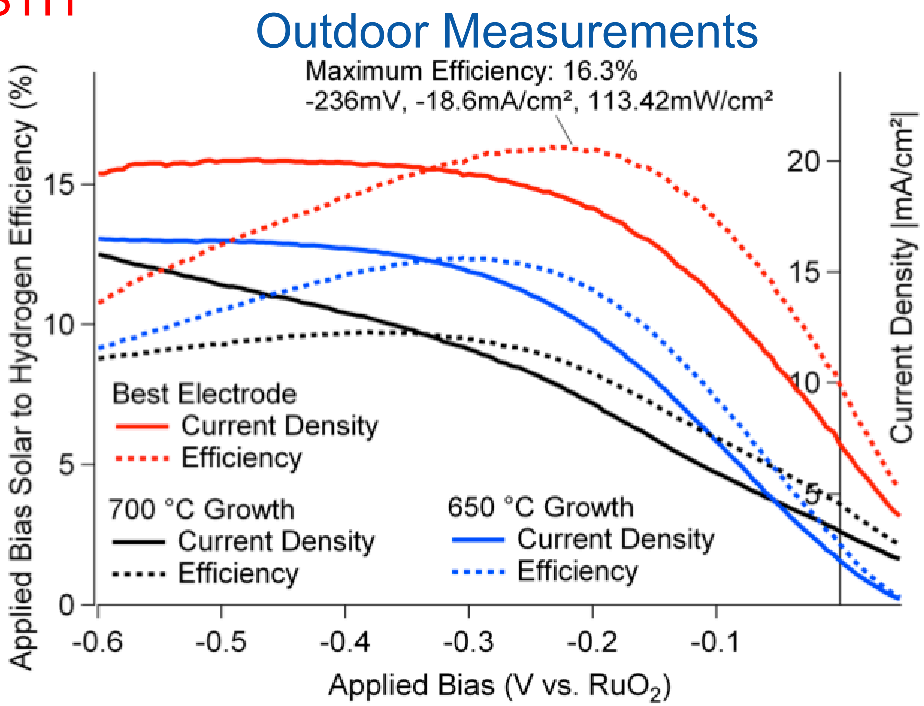
$GaInP_2/GaAs$ Tandem Cells

- Metal Organic Chemical Vapor Deposition synthesis
  Science, 1998, **280**, 425.
- 12.4% Solar to hydrogen efficiency (STH)
  - With Pt-black counter electrode
  - More active RuO_2 improves efficiency



New results demonstrate potential for 16.3% STH





Light (only) Driven Water Splitting

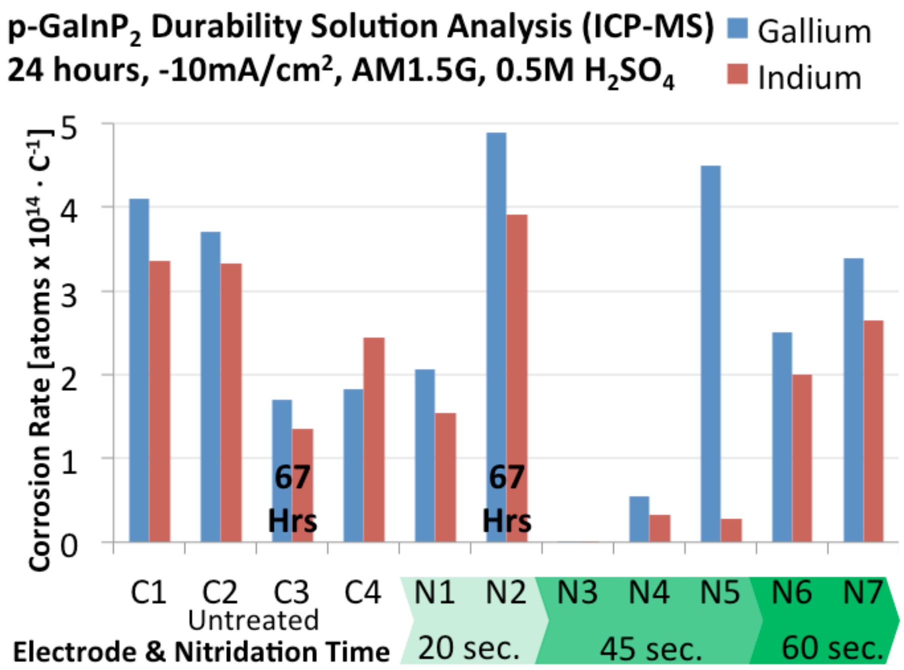
Video

Technical Accomplishments and Progress

Protection strategies for high-efficiency III-V photoelectrodes

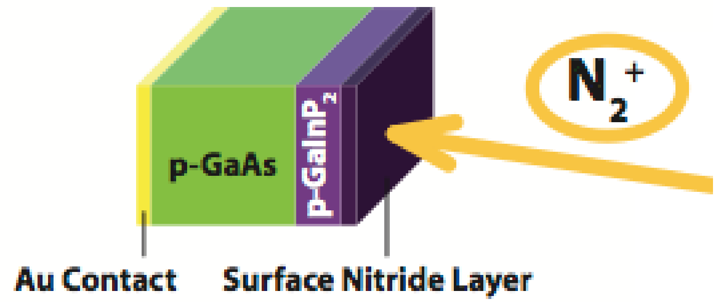
Electrochemical nitridation of p-GaInP$_2$

- Surface protected when run for 24 hours in pH1 $(NH_4)_2SO_4$
- XPS found NH_3 on surface
- XPS depth profiles
  - Unprotected surface was indium enriched and Ga deficient
  - Sample run in $(NH_4)_2SO_4$ had surface similar to as-grown (bulk)



Ion bombardment nitridation of p-GaInP$_2$

- Prevented decline in photocurrent as compared to untreated sample run for 24 hours
- 45-second bombardment led to reduced amount of Ga and In found in durability solution (by ICP-MS) (right)



Plasma nitridation of p-GaInP$_2$

- Hydrogen and nitrogen plasma of surface
- Preliminary data looks promising

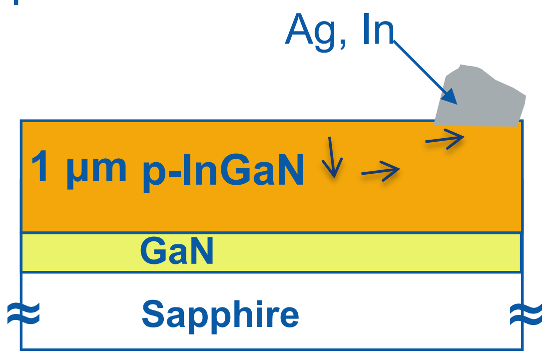
Technical Accomplishments and Progress

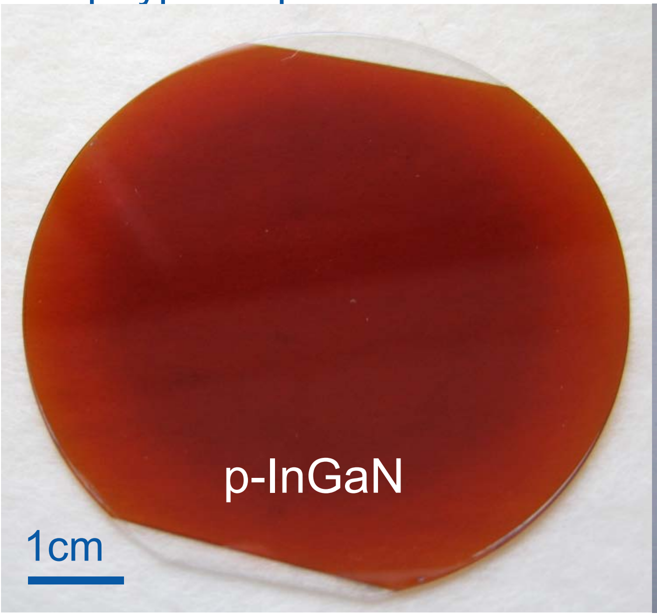
New materials development with potential for high efficiency and durability

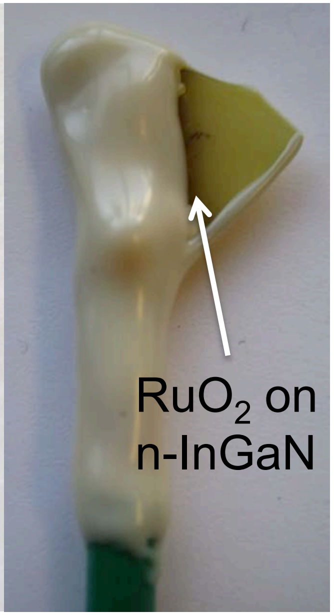
$In_xGa_{1-x}N$: III-V nitride materials (Los Alamos)

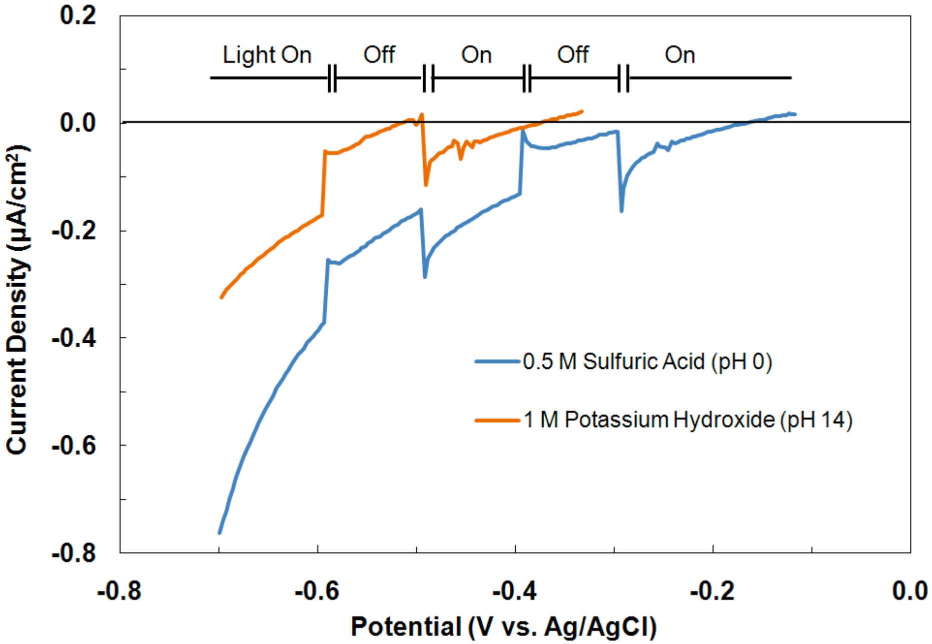
- LANL synthesized (MBE) full range of In:Ga compositions
- n-InGaN (previously)
  - stable single junction (non-tandem) material capable of water splitting
- p-InGaN with 2.2eV band gap (on sapphire)
- Developing and optimizing contacts, goal is conductive substrates
- Initial testing (open-circuit potential, photocurrent) demonstrated p-type response

Low photocurrents due to poor carrier collection









Technical Accomplishments and Progress

Amorphous materials with potential for low-cost high volume manufacturing

Hybrid tandem PV(a-Si)/PEC(a-SiC) thin-film devices

– MVSystems Inc. designs and synthesizes samples, PEC characterizations performed by NREL

– p-type photocathode materials

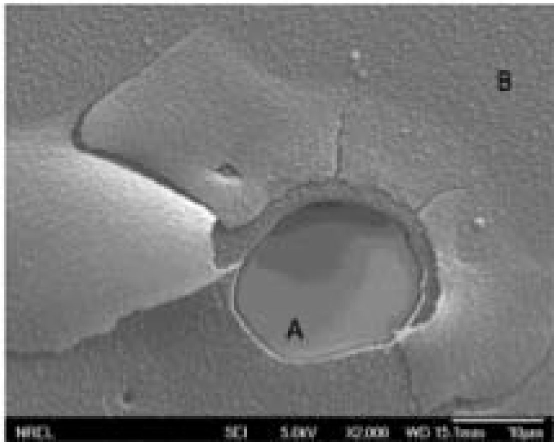
– Good stability over 300-hours at low current density (-1mA/cm^2) in pH2 buffer (right, above)

before testing

after testing

– SEM images show pinholes after 117 hours in pH 10 buffer (-0.3mA/cm^2) (right, below)

- EDS of “A” detects only Si, O, Na (glass)
- Area “B” composed of Si, C, O (semiconductor)



– Capable of unbiased water splitting

- -1.3 mA/cm^2 under simulated AM1.5 G
- 1.6% solar-to-hydrogen efficiency
- Room for improvement (3-5%)

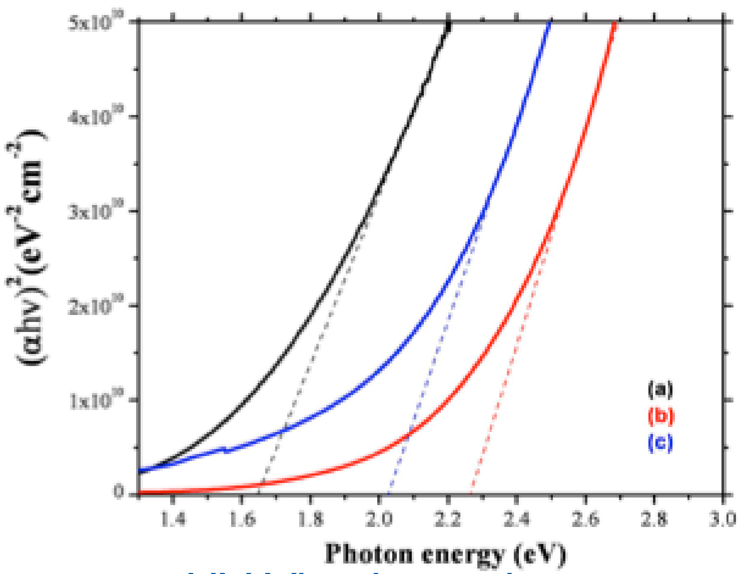
See talk PD053 for more detailed results and progress

Technical Accomplishments and Progress

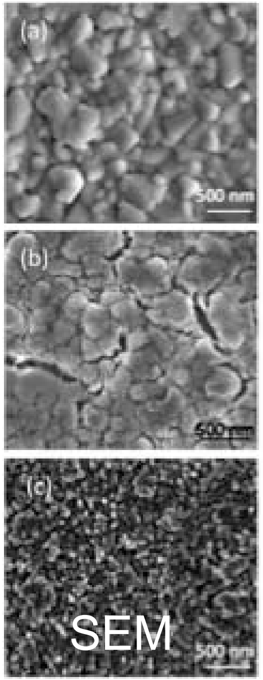
Efficient thin film chalcopyrite materials based on [Cu(In,Ga,Al)(S,Se,Te)$_2$]

$CuAlTe_2$ films synthesized by thermal evaporation in glove box

- Direct transition band gap in visible region
- EDS detected oxygen contamination
  - DFT predicts oxygen kills hole transport (right)
- Unstable in PEC environment
  - Not viable as synthesized



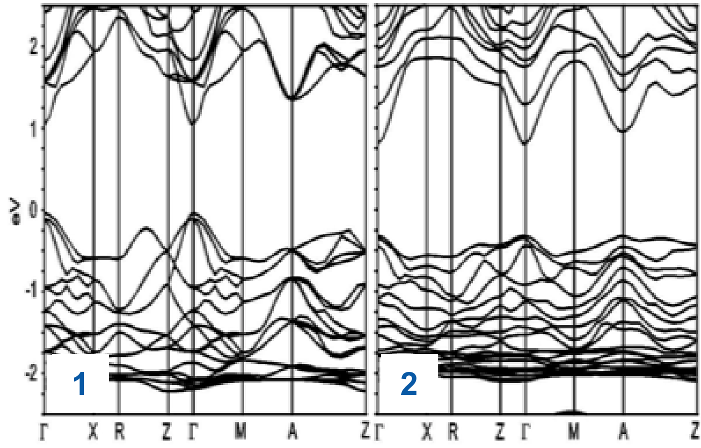
UV-Vis absorption



(a) and (b), co-evaporated (c) alternated layers of single elements. Films (b) and (c) underwent 450 ^{0}C post annealing for about 1 hour in vacuum

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



DFT calculated band structures for (1) $Cu_4Al_4Te_8$ and (2) $Cu_4Al_4Te_7O$

Technical Accomplishments and Progress

Theoretical screening of metal oxides semiconductors for photoelectrochemical hydrogen production

Oxide PEC (or PV) material is a potential game-changer for solar conversion

- 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

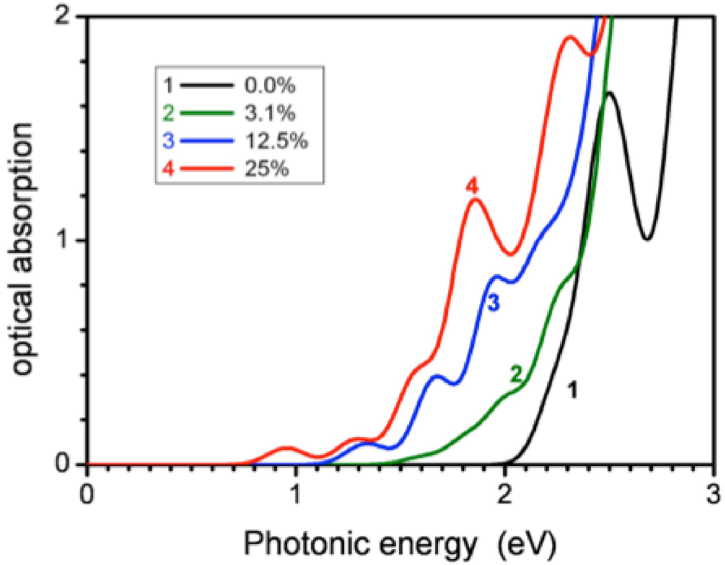
Discovery feedback loop

Technical Accomplishments and Progress

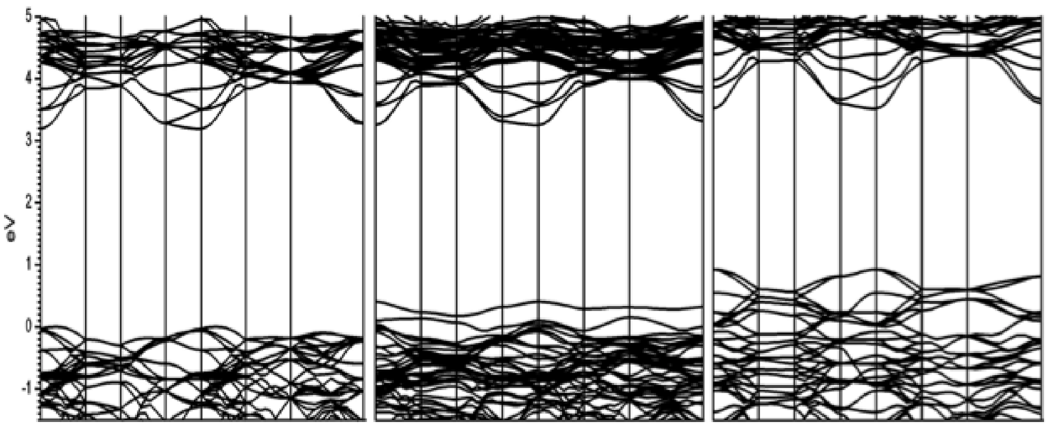
Theoretical screening of metal oxide materials

DFT calculations (at NREL) of absorption in TiO_2

- Want to reduce band gap and enhance absorption
- N 2p band lowers band gap
- Increasing N leads to reduced h^+ effective mass and better mobilities
- DFT has difficulty predicting actual band gap (TiO_2 E_g =3.2eV), however, trends follow prediction



Calculated generalized gradient approximations (GGA) optical absorption spectra (above) for pure TiO_2(1) and (Ta, N) co–incorporated TiO_2 with (2) 3.1%, (3) 12.5%, and (4) 25% of O replaced by N



Pure TiO_2 **(Ta, N) 3.1%(O)** **(Ta, N) 12.5%(O)**

See poster PD052

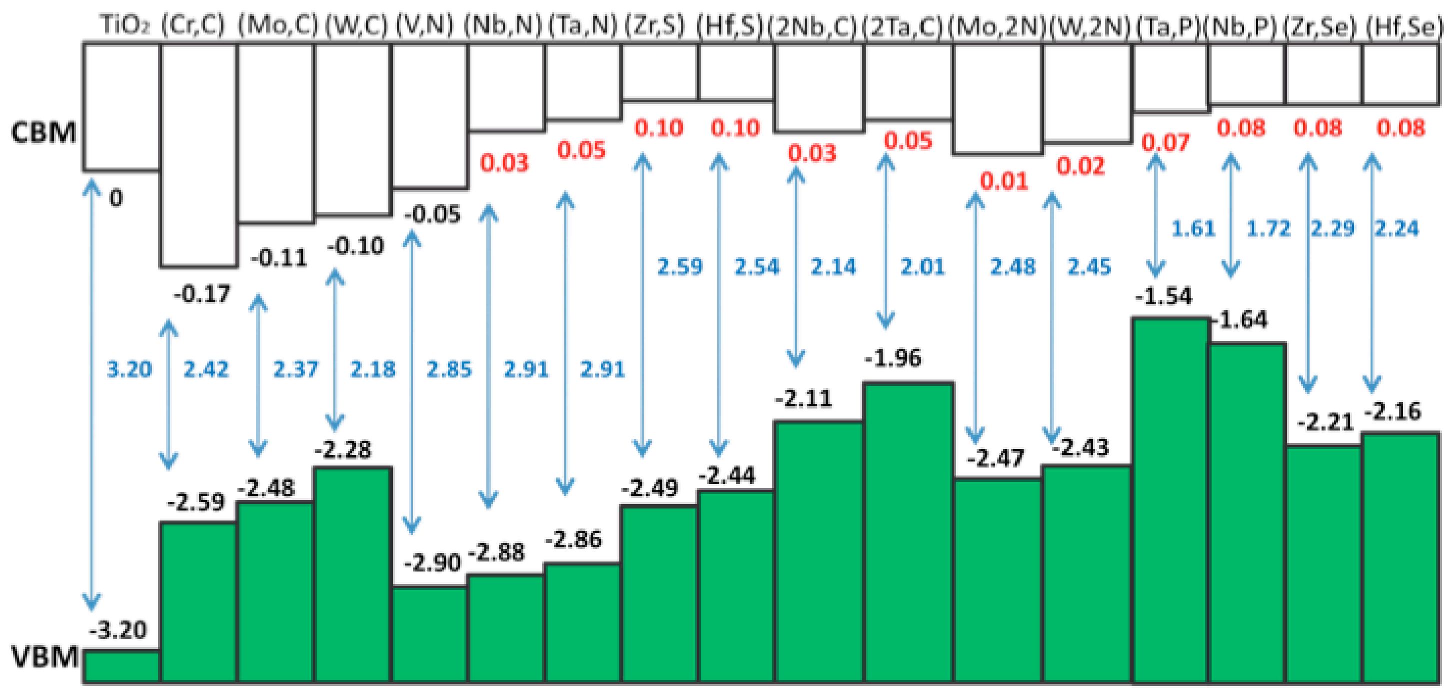
Technical Accomplishments and Progress

Theoretical screening of metal oxide materials

DFT calculations of conduction band minima (CBM) and valence band maxima (VBM) TiO_2

- Want to reduce band gap
- Need to shift CBM up (to be higher than H^+/H_2 reduction half-reaction potential)
- Full band structures needed to determine absorption and carrier mobility

Calculated GGA band offsets (at the Γ point) for TiO_2 and TiO_2 alloyed with various donor-acceptor combinations in the low-concentration regime. The CBM of pure TiO_2 is set to 0 as the reference and the band gap is corrected using a scissor operator



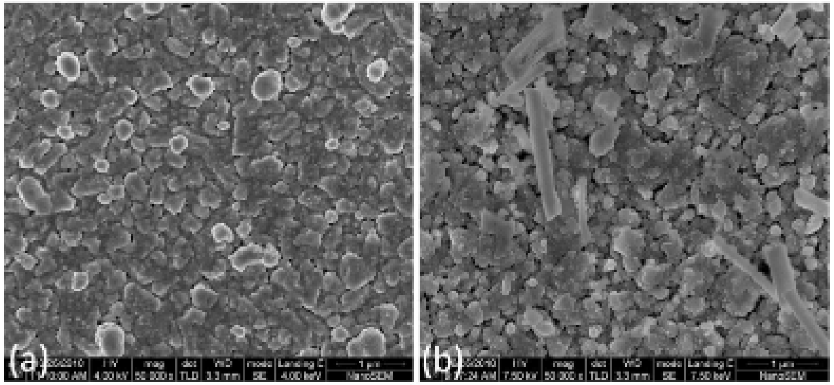
See poster PD052

Technical Accomplishments and Progress

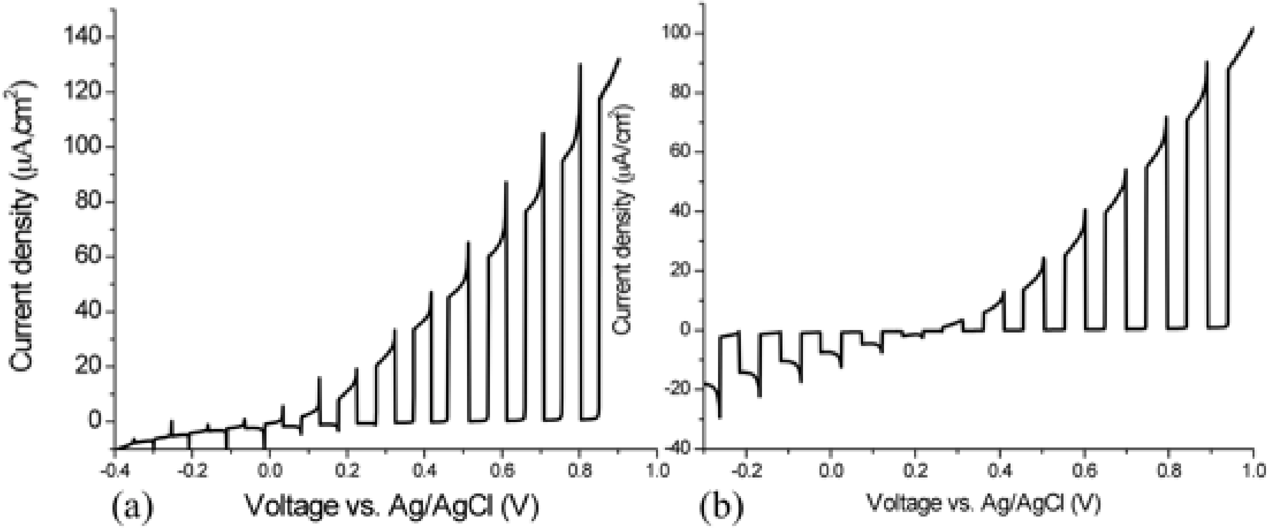
NREL synthesis of metal oxide alloy thin films

Synthesized $BiVO_4$ by co-evaporation

- XRD showed monoclinic phase (good)
- Higher temp led to porous and nanostructured films
- Characterized $BiVO_4$ synthesized by co-evaporation
- Fairly low n-type photocurrents observed in 1:1 Bi:V film
- Increasing the Bi:V ratio led to compensated (both p and n) behavior (bad)



SEM of monoclinic $BiVO_4$ after annealing at (a) 280°C for 20 minutes (b) 325°C for 1 hour



Chopped light I-V curves of $BiVO_4$ (left) with Bi:V = 1:1 and (right) Bi:V = 1.1:1 in pH7 1M Na_2SO_4

Technical Accomplishments and Progress

PEC Standards group

- 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 and presented results and process at**
    - SPIE Optics & Photonics Conference, San Diego, CA, August 2010
    - Spring MRS Meeting, San Francisco, CA, April 2011
- 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

Accomplishment of Program Milestones

Milestone	Due date	Status
Complete, with LLNL and UNLV, the collaborative work plan for the III-V materials systems "Surface Validation Study" which combines the ab-initio molecular dynamics theory with advanced synthesis and spectroscopic characterization techniques for developing corrosion mitigation schemes for achieving >100 hour operational durability in III-V materials systems capable of >10% STH conversion efficiency. (leading to DOE long-term targets of 10% STH efficiency and 5000 hour durability.)	1/15/11	Completed
Complete absorption, PEC efficiency and stability characterizations of nanostructured molybdenum disulfide and tungsten disulfide PEC photocatalysts with demonstrated quantum-confined bandgaps in the 1.2eV to 1.8eV range.	4/15/11	Completed
Complete experiments on PEC photoelectrodes made from InGaN grown on conductive substrates to determine durability benchmarked against a 100 hour operational lifetime target.	9/1/11	On-track
Complete initial spectroscopic studies with UNLV on III-V materials systems as part of the collaborative "Surface Validation Study". Use results to design corrosion mitigation schemes for achieving >100 hour operational durability in III-V materials systems capable of >10% STH conversion efficiency.	9/30/11	On-track

To date, all program milestones have either been met or are on-track for on-time completion.

Collaborations

Partners (extensive collaboration with all)

- University of Nevada Las Vegas
  - Samples characterized (aged) at NREL and sent to Heske group for X-ray spectroscopic characterization both at UNLV and the Advance Light Source to identify corrosion intermediates and products
  - Key partner in surface validation project (PD051)
- Lawrence Livermore National Laboratory
  - Ogitsu group uses molecular dynamic simulations and theoretical calculations coupled with observations from UNLV analysis to elucidate corrosion mechanism
  - Key partner in surface validation project (PD058)
- Colorado School of Mines
  - Graduate and undergraduate research associates; electron microscopy and XPS user facilities; sample treatments and exchange
- University of Colorado
  - Undergraduate research associates
- University of Hawaii
  - $CuGaSe_2$, and RuO_2 from Hawaii for Pt catalyst studies; WO_3 from Hawaii for dual photoelectrode testing; cooperative PEC characterization; sample exchange and validation (PD053)
- Stanford University
  - Jaramillo group- subcontract on quantum confined nanostructured transition metal dichalcogenides (PD033); overlapping undergraduate research associates

Collaborations

Partners (extensive collaboration with all)

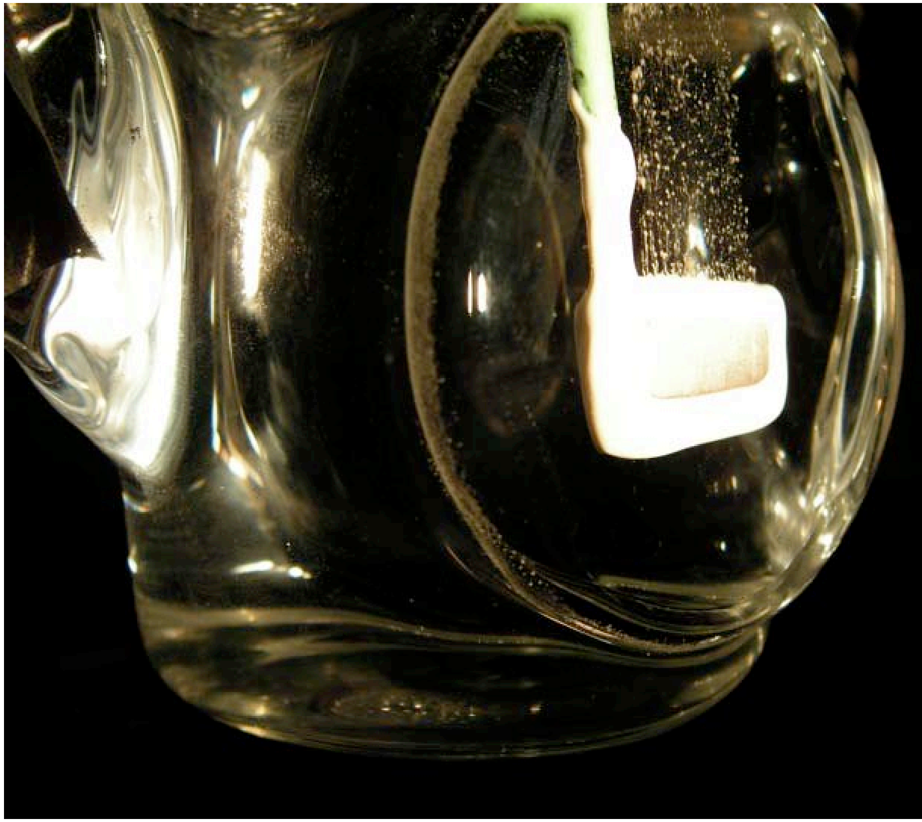
- University of Louisville
  - Sunkara group- ALD of TiO_2 on $GaInP_2$
- Los Alamos National Laboratory
  - Todd Williamson synthesizes InGaN samples
- Small Business Innovation Research
  - Synkera Technologies, Inc. (Industry)
    - We provide PEC characterization of novel electrode structures and materials obtained from our collaborator (PD062)
  - Physical Optics Corp. (Industry)
    - We provide logistical support, consulting, and PEC characterization of untested materials obtained from our collaborator (PD061)
- Program production solicitation
  - MVSystems, Inc. (Industry)
    - We provide characterization and durability analysis of a-SiC:H obtained from our collaborator (PD053)

Proposed Future Work

- Investigate MBE grown p-InGaN on conductive substrates
  - p-type for cathodic protection
  - Conductive substrates for improved efficiency
- Work with surface validation team partners (UNLV, LLNL) to test, evaluate, and understand corrosion mechanism on III-V materials and develop protection strategies
- Evaluate protective coatings and treatments for proven high-efficiency materials that suffer from instability
  - Thin coatings by ALD
  - Electrochemical nitridation
  - Plasma nitridation
  - Ion bombardment nitridation
- Characterize emerging polycrystalline thin-films for stability and efficiency
  - Cu_2ZnSnS_4
  - $CuGaSe_2$
- Synthesis and characterization of oxide materials
  - Cu-Ti-O system
  - High-alloy content co-doped TiO_2
- Outdoor testing of dual photoelectrode configurations
  - Si, $GaInP_2$, $CuGaSe_2$ photocathodes
  - WO_3, Fe_2O_3, $BiVO_4$ photoanodes

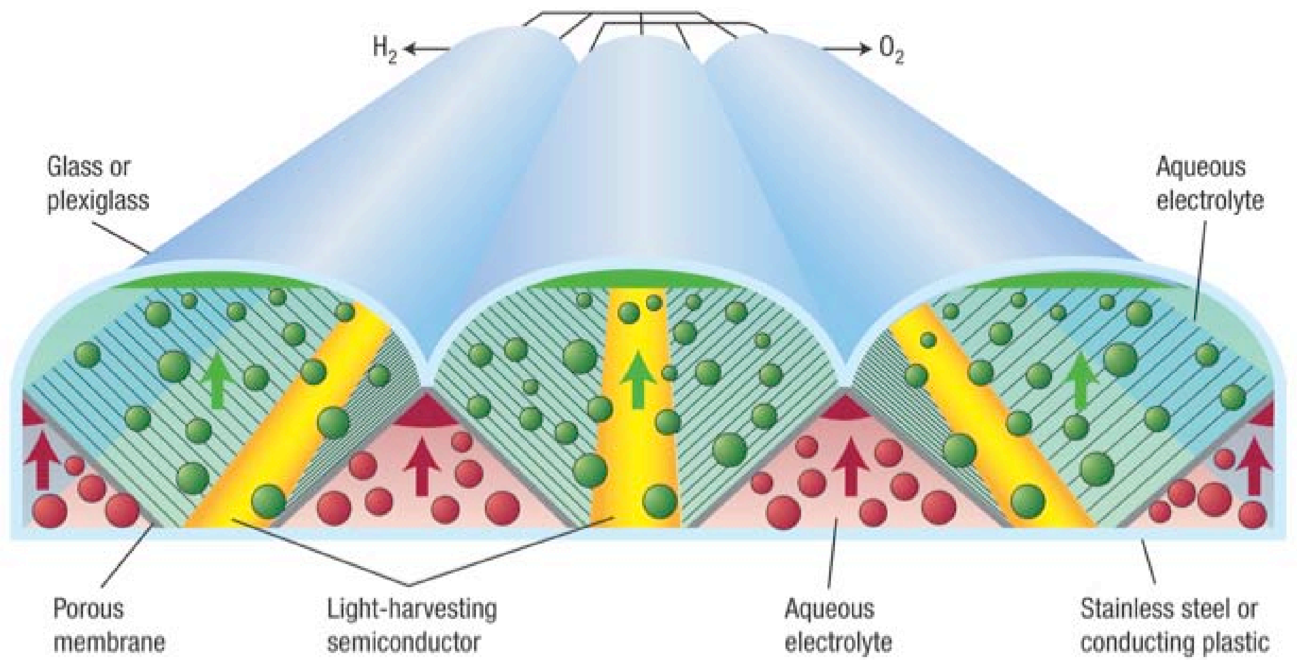
Summary

- Improved overall water splitting efficiency of world-record holder by using more active oxygen evolution counter electrode (RuO_2)
- Developed potential protective treatments for high-efficiency III-V photoelectrodes (nitridation)
- Synthesized and characterized metal oxide semiconductors ($BiVO_4$) and calculated optical and electronic properties of co-doped TiO_2 that we plan to make
- Provided advice and characterization services to three industrial partners
- Continued 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 working material; secondary concern is developing a high-throughput/low-cost synthesis route



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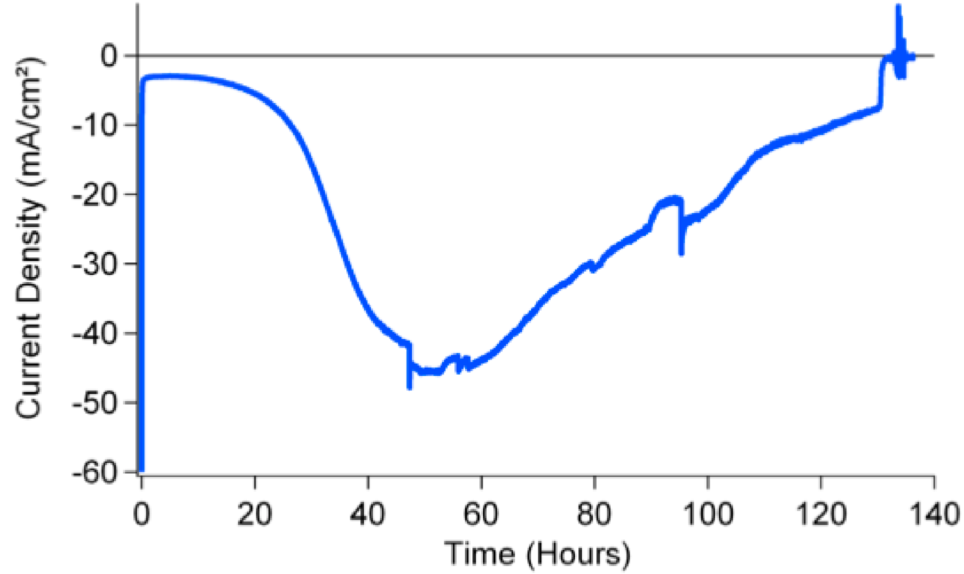
- Adam Welch- NREL
  - RuO_2 synthesis, $GaInP_2$ tandem efficiency, interference microscopy, SEM, a-SiC testing, videography, figure generation
- James Young- NREL
  - InGaN characterization
- Heli Wang - NREL
  - $GaInP_2$ electrochemical nitridation
- Avery E. Lindeman- Harvard University (intern)
  - $GaInP_2$ ion bombardment nitridation
- Yanfa Yan- NREL
  - Metal oxide theory & synthesis
- Todd Williamson- Los Alamos National Lab
  - InGaN synthesis

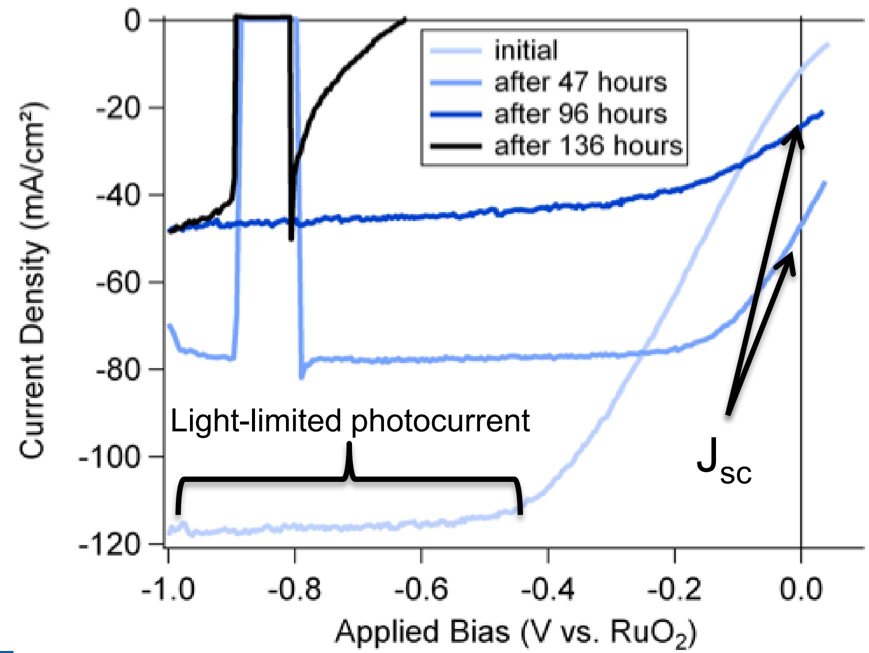
Technical Back-Up Slides

Tandem Cell Durability

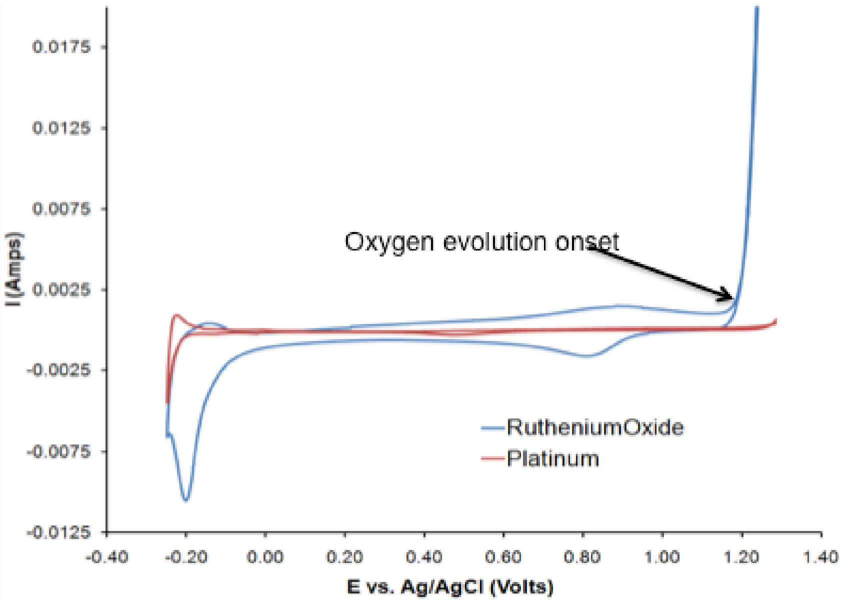
- Operated at zero bias, RuO_2 CE, 0.5M H_2SO_4 with fluorosurfactant, 10 suns from xenon lamp (above, right)
- Efficiency increased until 55 hours, then declined until failure at 132 hours
  - Failure due to gaping hole, likely an intrinsic defect



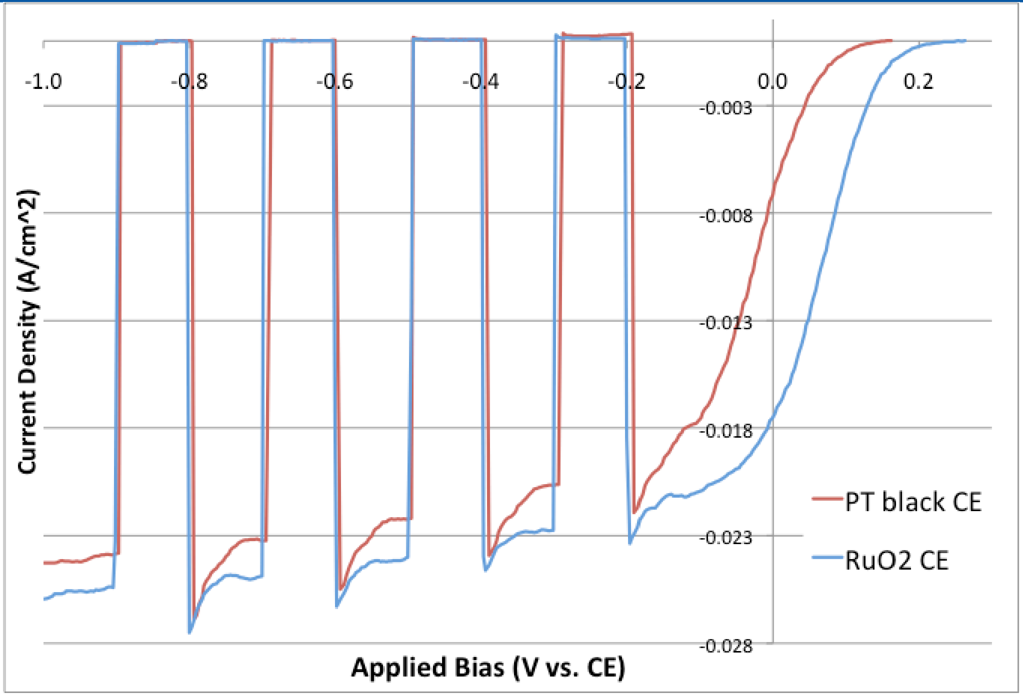
- Two electrode J-V shows decline in light-limited photocurrent under reverse bias but an initial improvement in short-circuit current density (J_{sc})

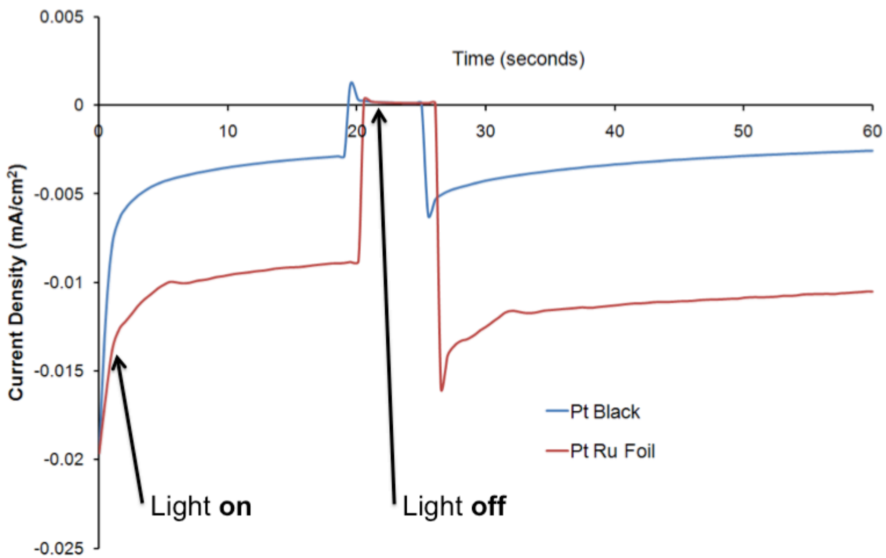


Oxygen Catalysts for Optimized System



CV of ruthenium oxide on a platinum foil vs. platinum foil, in 0.5M sulfuric acid





Short circuit current measurement using the same tandem cell as the photocathode, comparing a platinum black counter electrode to a ruthenium-oxide coated platinum counter electrode. The cell was illuminated at AM1.5 G, and the electrolyte was fresh 0.5M sulfuric acid with 2g/L of Zonyl FSN-100 as surfactant