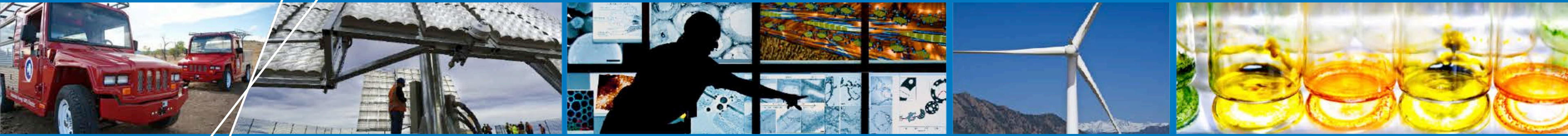
Semiconductor Materials for Photoelectrolysis



2013 U.S. DOE Hydrogen & Fuel Cells Program Review

Todd G. Deutsch, John A. Turner,

May 16th, 2013

Project ID: PD035

Overview

Timeline

- **Project start date: 2004**
- **Project end date: 9/2013***
- **Percent complete: 90%**

Budget

- **Total project funding**
  - DOE share: $9.8M
- **Funding received in FY12: $1100k****
- **Planned funding for FY13: $720k**

* Project continuation and direction determined annually by DOE

** Includes UNLV, SU and UTA support

Barriers

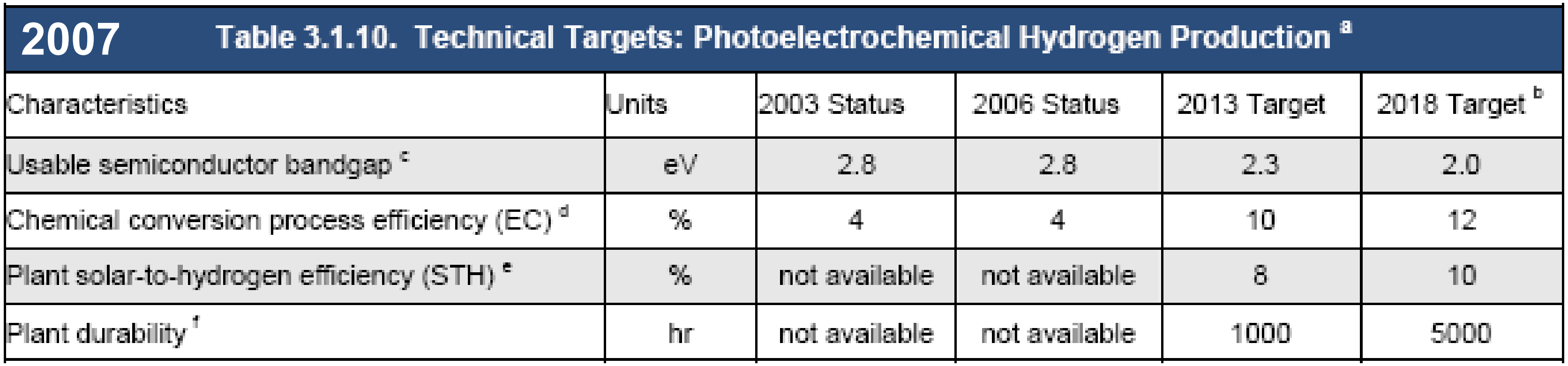
- **Barriers addressed**
  - AE. Materials Efficiency –Bulk and interface.
  - AF. Materials Durability. – Bulk and interface
  - AG. Integrated Device Configurations
  - AI. Auxiliary Materials

Partners

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

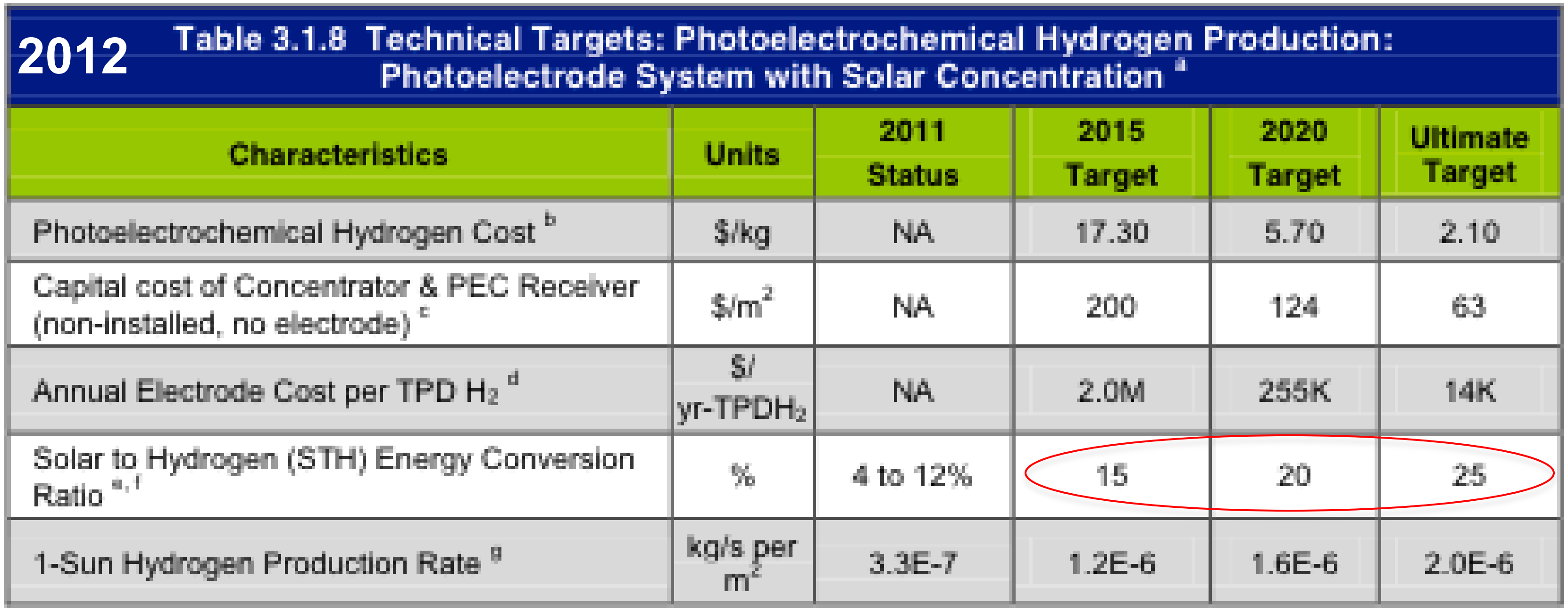
Relevance

Old technical targets vs. new technical targets



2007 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



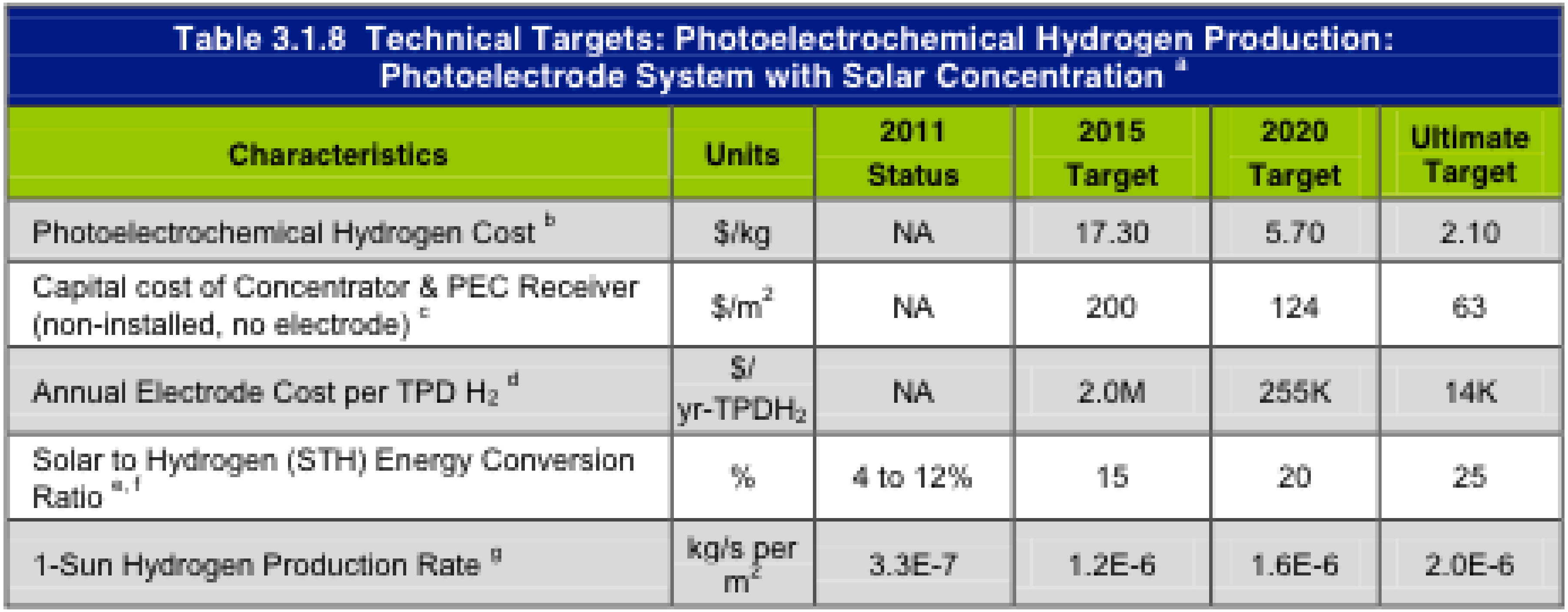
2012 Table 3.1.8 Technical Targets: Photoelectrochemical Hydrogen Production: Photoelectrode System with Solar Concentration [a]

Characteristics	Units	2011 Status	2015 Target	2020 Target	Ultimate Target
Photoelectrochemical Hydrogen Cost [b]	\$/kg	NA	17.30	5.70	2.10
Capital cost of Concentrator & PEC Receiver (non-installed, no electrode) [c]	\$/m²	NA	200	124	63
Annual Electrode Cost per TPD H_2 [d]	\$/yr-TPDH_2	NA	2.0M	255K	14K
Solar to Hydrogen (STH) Energy Conversion Ratio [e, f]	%	4 to 12%	15	20	25
1-Sun Hydrogen Production Rate [g]	kg/s per m²	3.3E-7	1.2E-6	1.6E-6	2.0E-6

http://www1.eere.energy.gov/hydrogenandfuelcells/mypp/pdfs/production.pdf

Relevance

- The objective of this work is to develop low band gap semiconductor material devices that can split water into hydrogen and oxygen spontaneously upon illumination with a minimum of 10% efficiency
- The main focus this past year has been to work with state-of-the-art III-V materials that **meet DOE's near-term efficiency targets and optimize surface treatments that promote durability**.



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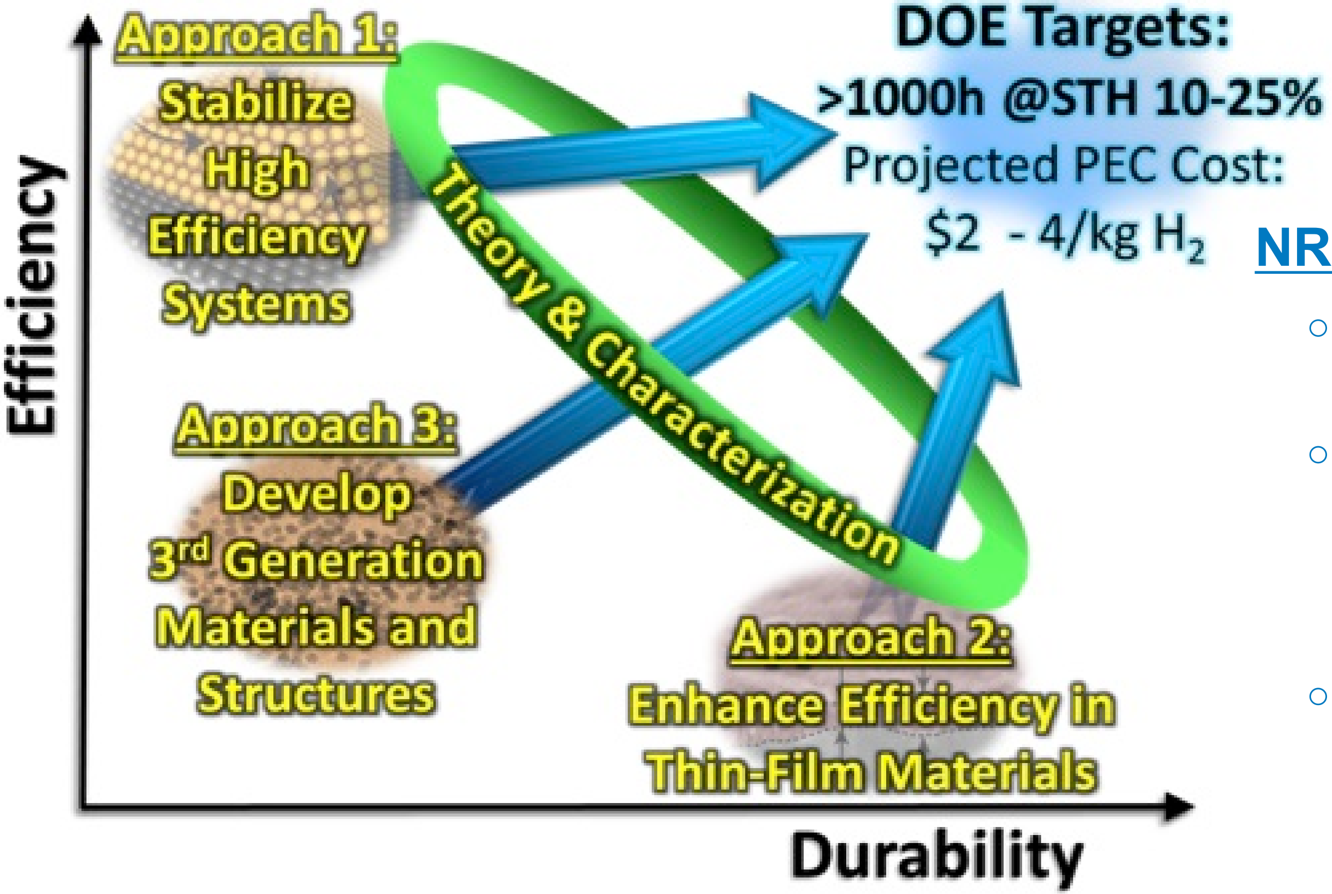
1-Sun Hydrogen Production Rate [g]	kg/s per m^2	3.3E-7	1.2E-6	1.6E-6	2.0E-6

Approach

The US DOE PEC Working Group approach towards efficient and durable solar H_2 production



Approach 1: Stabilize High Efficiency Systems

Approach 2: Enhance Efficiency in Thin-Film Materials

Approach 3: Develop 3rd Generation Materials and Structures

Theory & Characterization

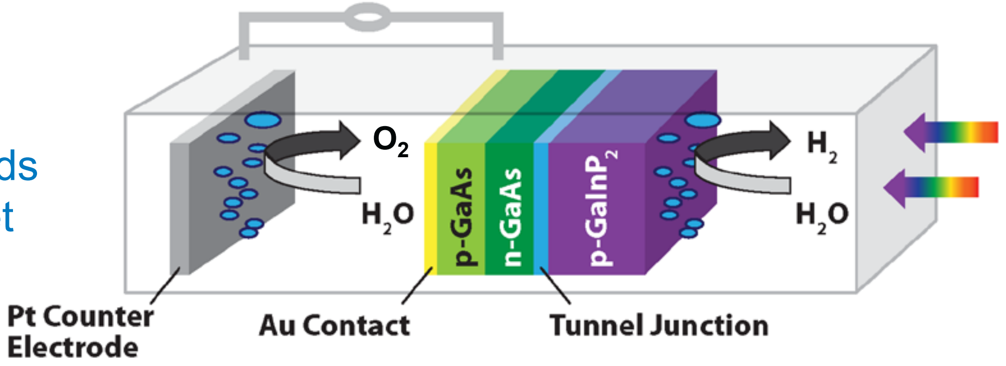
DOE Targets:
>1000h @STH 10-25%
Projected PEC Cost:
\$2 - 4/kg H_2

NREL-led Project Focus:

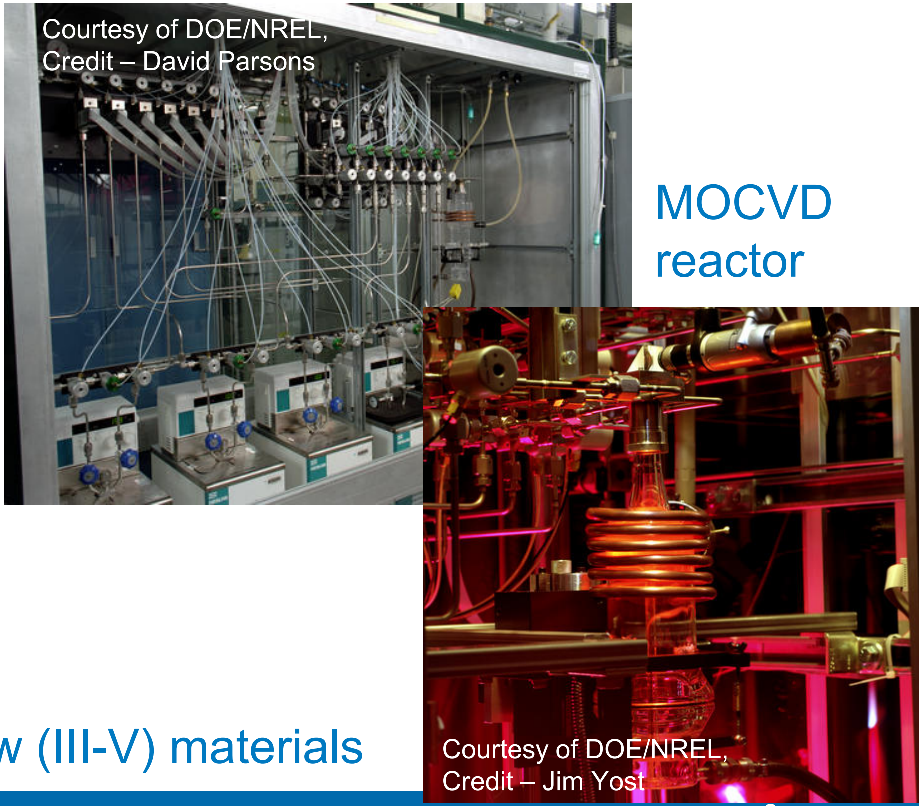
- Extend durability of highly efficient materials
- Ensure efficiencies are maintained and not compromised by durability treatments
- Investigate new materials that can achieve ultra-high future efficiency goals

Approach: Engineering Known Materials

Enhancing durability of $GaInP_2$/GaAs tandem system through material engineering



- **High efficiency**
  - Only demonstrated system that exceeds unbiased 10% solar-to-hydrogen target
    - 12.4% with Pt-black counter electrode, >16% with RuO_2 CE at moderate bias
  - Metal organic chemical vapor deposition (MOCVD) synthesis
    - Synthesis by NREL's III-V team
- **Focus: optimize stability treatment**
  - Ideal system for observing and modeling corrosion
  - Can tolerate efficiency losses due to protective treatment and still meet 10% target
- **III-V cost barriers are falling due to innovative synthesis routes**



Courtesy of DOE/NREL, Credit – David Parsons

MOCVD reactor

Courtesy of DOE/NREL, Credit – Jim Yost

New technical targets for efficiency require new (III-V) materials

Approach: Surface Validation Team

Partner with specialists that have unique expertise and resources

Detailed spectroscopic measurements to observe and understand the chemistry of the surface and near-surface of III-V ($GaInP_2$)

- **Heske group at UNLV**
  - XPS, XAS, XES, IPES, UPS, AFM
    - Some measurements at Advanced Light Source (ALS)
  - Snapshots of surface pre-, intermediate, post-exposure
  - Identify common features of and conditions that lead to corrosion
  - **Characterize stabilized surfaces**

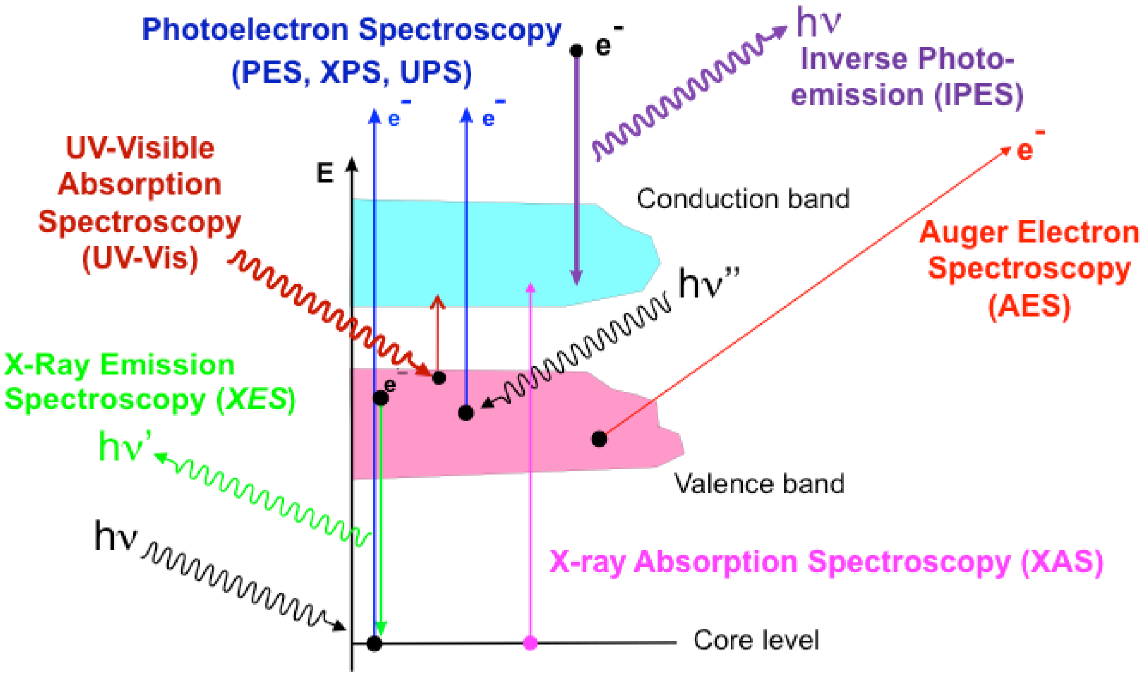


Diagram courtesy of Clemens Heske

Goals– Use combination of surface spectroscopy and theory to...

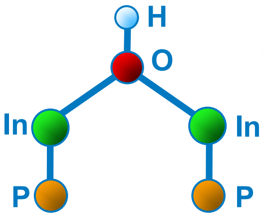
1. Study PEC corrosion in III-V's, the simplest (model) system to uncover corrosion initiation sequence and develop remediation strategy
2. Identify chemical character and mechanism of successful protective treatments
3. Apply lessons learned to other systems capable of high efficiency solar water splitting

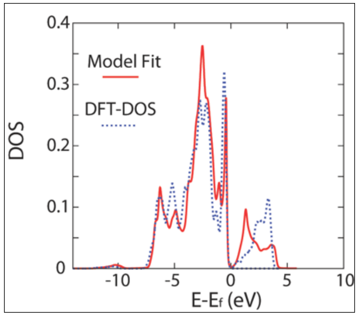
Approach: Surface Validation Team

Partner with specialists with unique expertise and resources

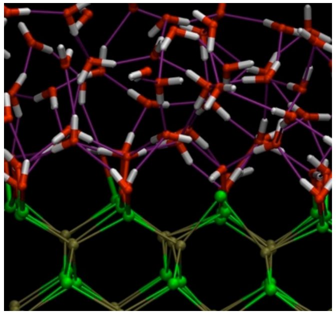
Theoretical modeling of the electronic structure of III-V ($GaInP_2$)

- **Partner with Ogitsu group at LLNL**
  - Calculate XAS and XES spectra to correlate experimental result with surface/near surface compositions
  - Ab initio molecular dynamics simulations
  - Model surfaces for mechanistic understanding of hydrogen evolution and corrosion





Courtesy of Woon Ih Choi and Brandon Wood (LLNL)



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1. Study PEC corrosion in III-V's, the simplest (model) system to uncover corrosion initiation sequence and develop remediation strategy
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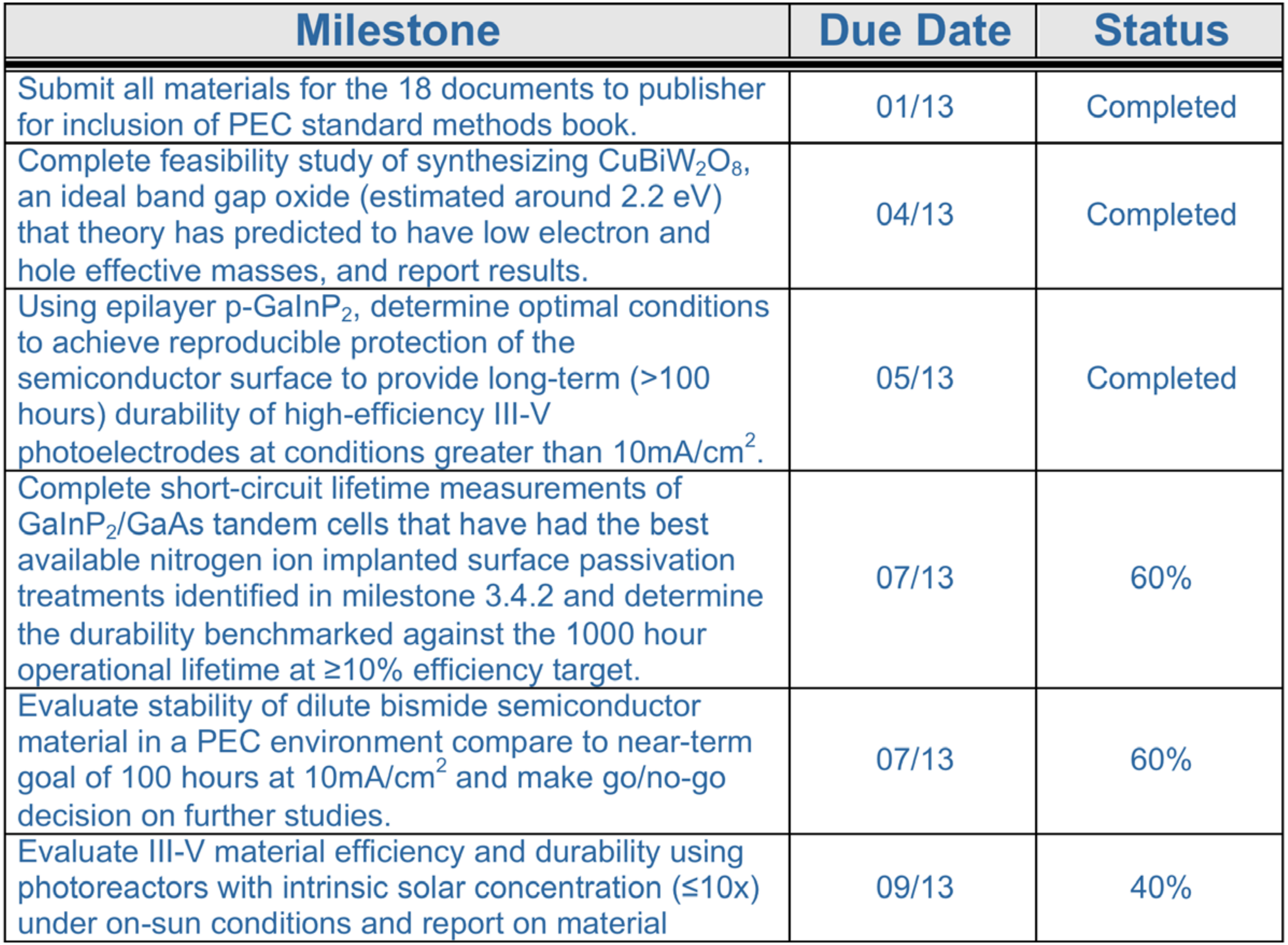
Approach – Milestones



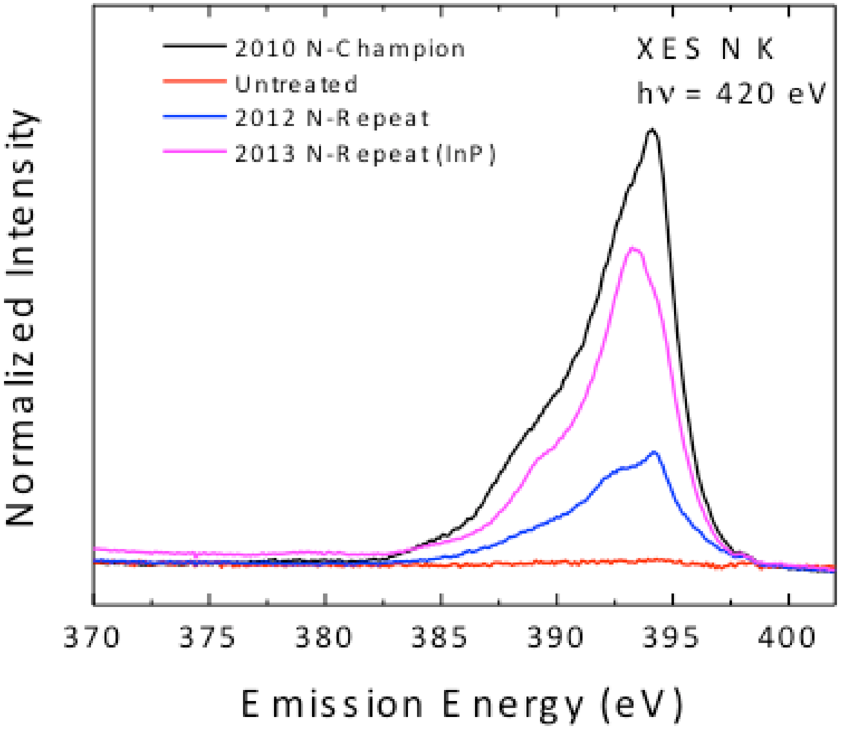
Milestone	Due Date	Status
Submit all materials for the 18 documents to publisher for inclusion of PEC standard methods book.	01/13	Completed
Complete feasibility study of synthesizing $CuBiW_2O_8$, an ideal band gap oxide (estimated around 2.2 eV) that theory has predicted to have low electron and hole effective masses, and report results.	04/13	Completed
Using epilayer p-$GaInP_2$, determine optimal conditions to achieve reproducible protection of the semiconductor surface to provide long-term (>100 hours) durability of high-efficiency III-V photoelectrodes at conditions greater than $10mA/cm^2$.	05/13	Completed
Complete short-circuit lifetime measurements of $GaInP_2$/GaAs tandem cells that have had the best available nitrogen ion implanted surface passivation treatments identified in milestone 3.4.2 and determine the durability benchmarked against the 1000 hour operational lifetime at ≥10% efficiency target.	07/13	60%
Evaluate stability of dilute bismide semiconductor material in a PEC environment compare to near-term goal of 100 hours at $10mA/cm^2$ and make go/no-go decision on further studies.	07/13	60%
Evaluate III-V material efficiency and durability using photoreactors with intrinsic solar concentration (≤10x) under on-sun conditions and report on material	09/13	40%

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

Technical Accomplishments – UNLV Spectroscopic Characterization

Collaboration with UNLV instrumental in identifying/optimizing nitrogen ion (N_2^+) treatment

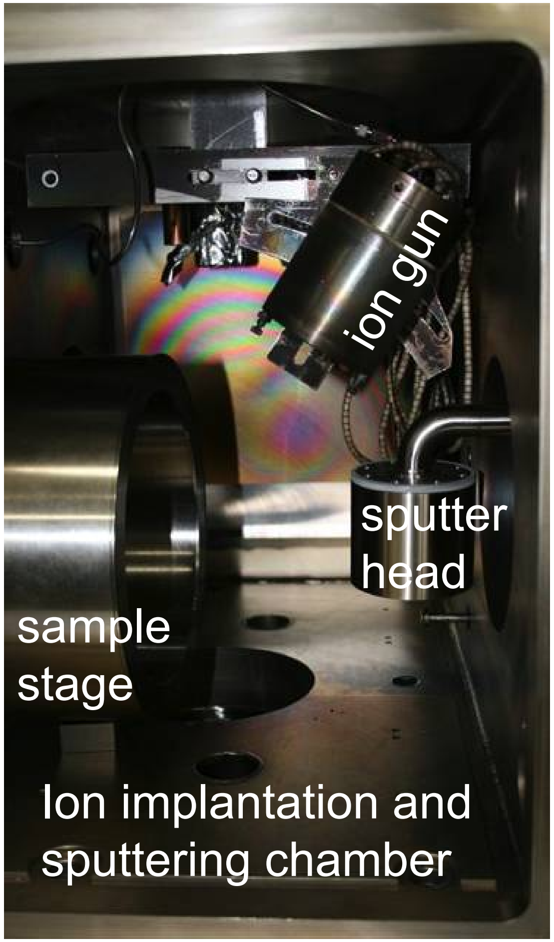
- **Identify conditions that led to successful nitride treatment**
  - After initial success, we were unable to reproduce the protective treatment
  - Breakthrough provided by UNLV allowed us to repeat stability treatment
  - XPS Survey showed enabling component of working treatment (unintentional metal contamination)
- **UNLV partners aid in optimizing nitride treatment conditions**
  - Nitride difficult to detect in dilute amounts by conventional techniques (low-Z element)
  - Significant time between original treatment and its repetition, ion-gun was abused
  - UNLV XES analysis at Advanced Light Source gives us feedback we need to tune our new ion source to achieve the level of nitride incorporation in original “champion” sample



- Synchrotron data collection by Michael Weir
- Analysis by Michael Weir, Lothar Weinhardt, Kyle George, Clemens Heske
- **Co-inventors on provisional patent application**

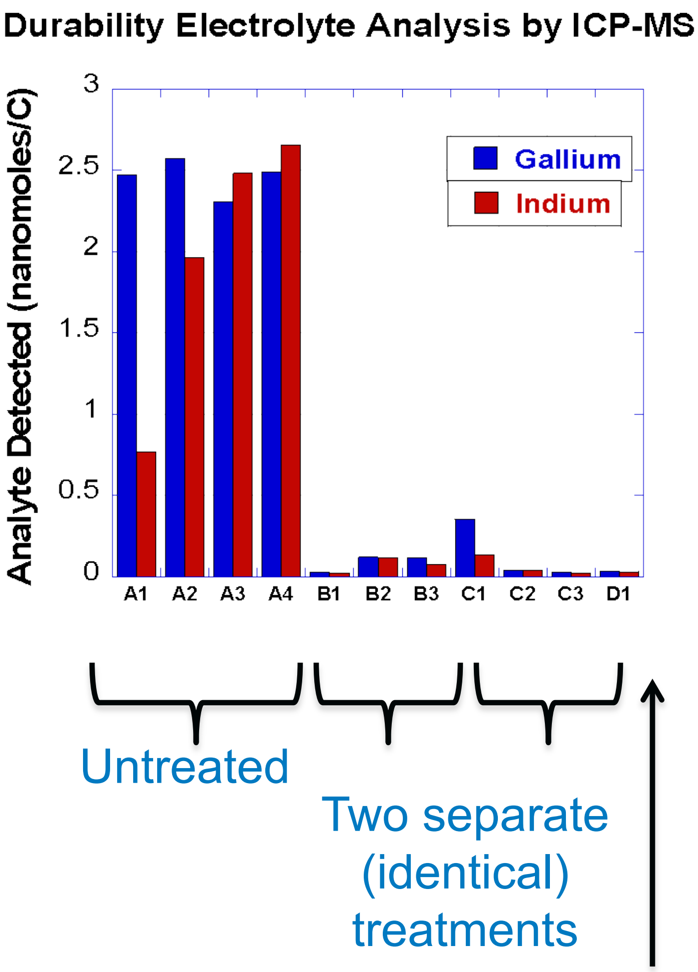
Technical Accomplishments – Reproduce Protective Treatment on $GaInP_2$

Trace amounts of Ga and In in corrosion solutions indicate a protected surface



Photoelectrode durability conditions

- 3M H_2SO_4 with fluorosurfactant
- AM1.5 G simulated light
- -10mA/cm^2 (12.3% STH equivalent) constant current applied
- 24 hours
- Tandem electrode conditions slightly different (constant V)



Untreated

Two separate (identical) treatments

Treated tandem

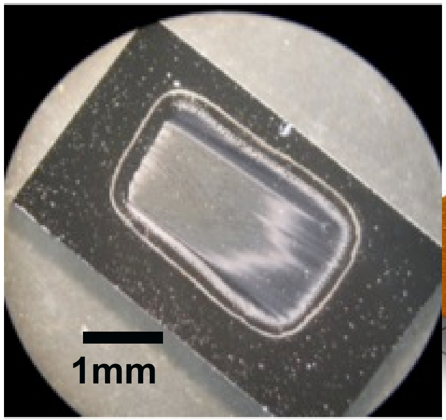
Feedback and analysis from UNLV identified enabling component of treatment (applied via sputtering) and allowed us to reproduce protective effect

Technical Accomplishments- Tandem Surface Protection

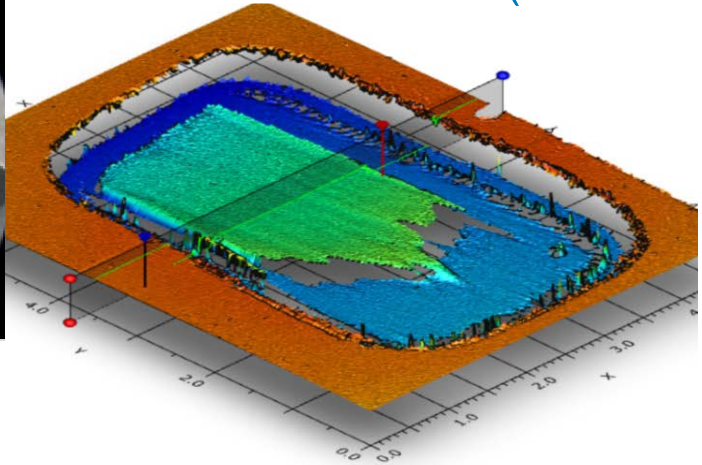
Progress in optimizing nitrogen ion (N_2^+) treatment: promising results at very high currents

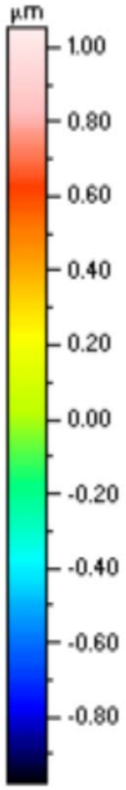
Control (untreated p-$GaInP_2$ epilayer) etched significantly (~1 µm)

- Constant current (-10mA/cm^2) for 24 hours in 3M H_2SO_4



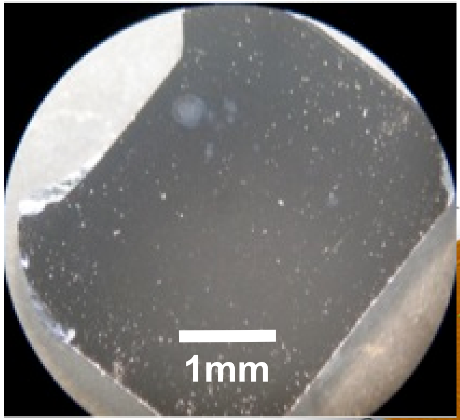
Control (no treatment)

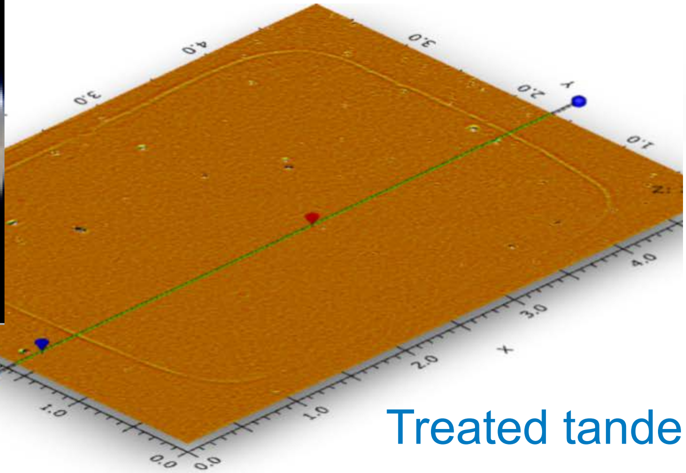




Tandem electrode (p-$GaInP_2$ on p/n-GaAs) had no detectable etching after 24 hours at about twice the current density

- Constant voltage (-1V vs Pt CE)
- Average ~ -18.5mA/cm^2
  - Equivalent flux of 23% efficiency
- Important step toward future devices
  - 25% STH under 10X light concentration ~200mA/cm^2

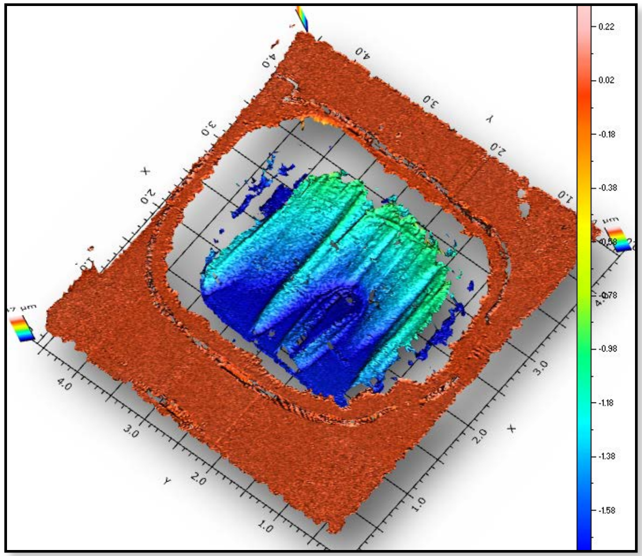




Treated tandem

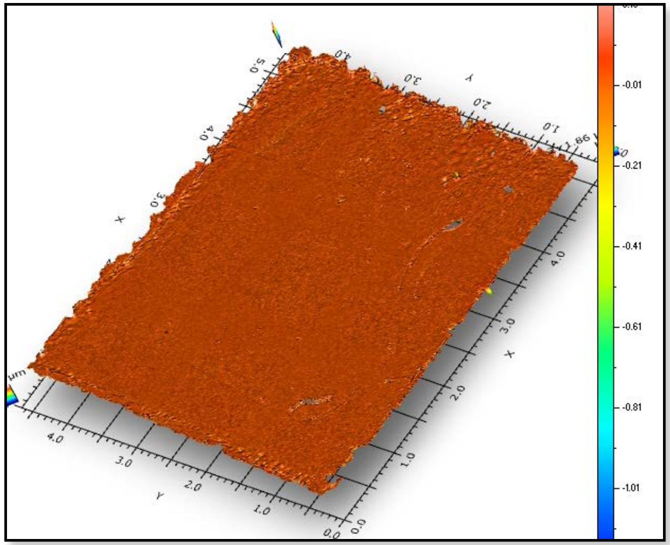
Technical Accomplishments-PEC Performance Maintained

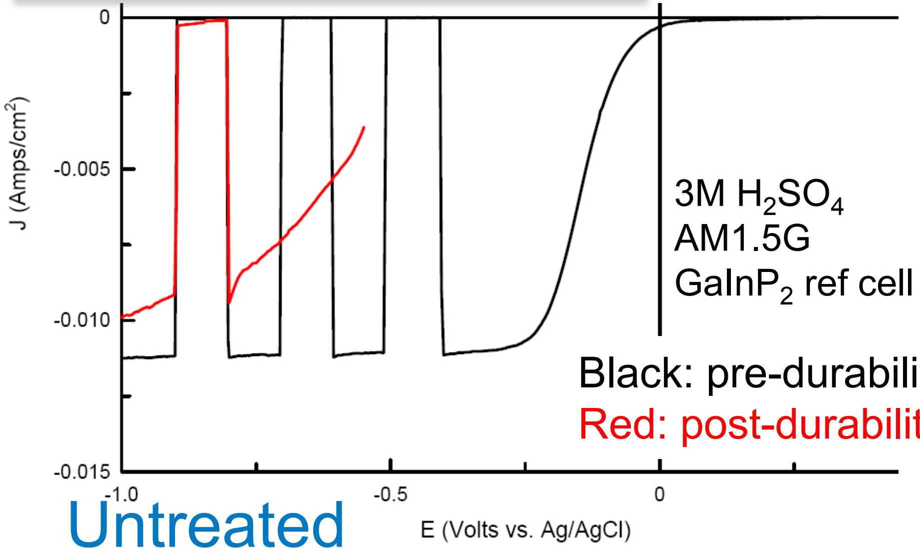
In addition to preventing physical degradation the nitrogen ion (N_2^+) treatment maintains PEC performance of p-$GaInP_2$ after 24 hours of durability testing at -10 mA/cm^2 in 3M H_2SO_4



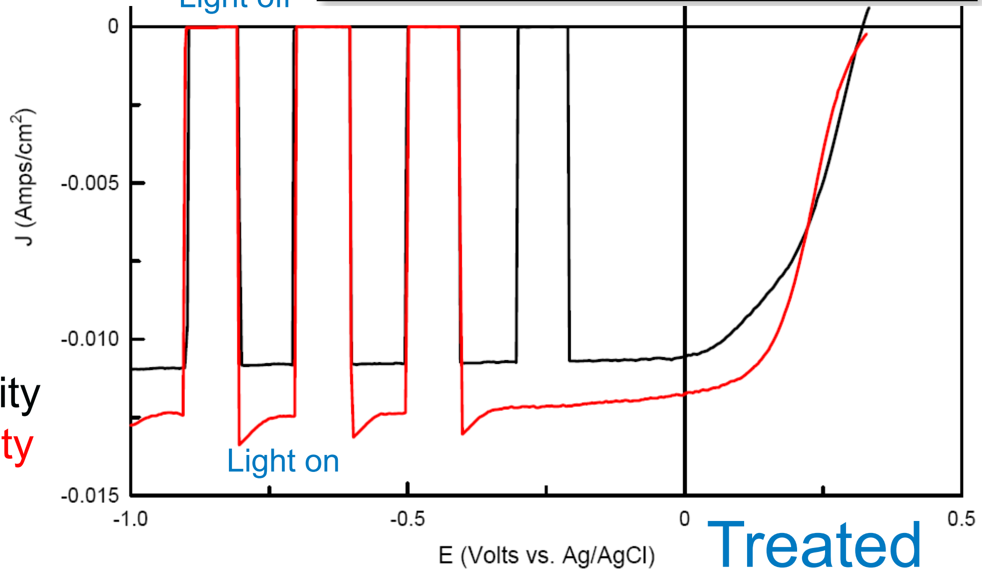
Treated and untreated samples have equivalent light-limited photocurrent magnitudes (no loss of efficiency).

Dark current, reduced photocurrent and shift in onset potential are indicative of corrosion.





Untreated



Treated

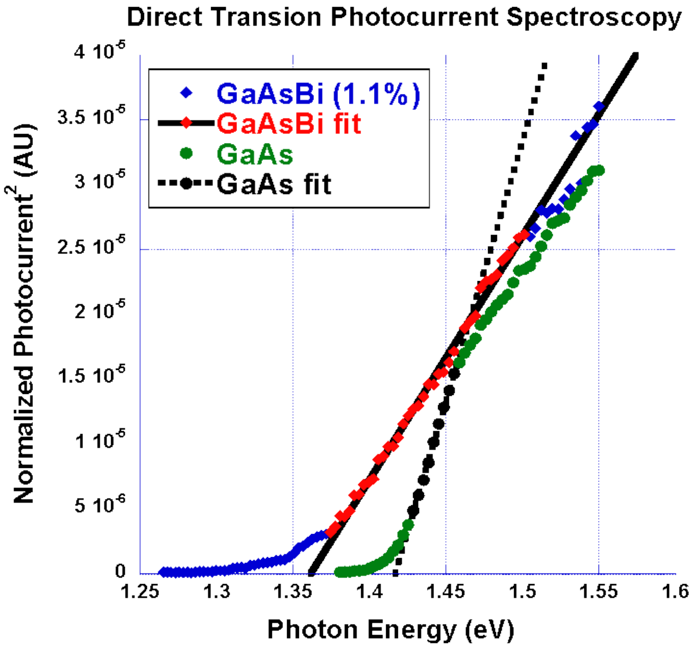
Technical Accomplishments – New III-V materials

Tandem materials with lower band gaps needed to meet 25% STH target – Optimal combination for stacked system is 1.6eV/0.9eV

- **Continued work to optimize $In_xGa_{1-x}N$ material system**
  - Continuously variable band gap between 3.4 eV (GaN) and 0.7 eV (InN)
  - Samples synthesized by molecular beam expitaxy at LANL by Todd Williamson
  - Poster PD097
- **Dilute Bismides ($GaAs_{1-x}Bi_x$)**
  - Incorporating bismuth in to GaAs during growth lowers the E_g from 1.42 eV without significant loss in electron and hole mobility
  - Samples synthesized by molecular beam epitaxy at NREL by Aaron Ptak
- **Tandem absorber considerations**
  - Band gap – E_g (eV)
    - Lower band gap utilizes greater portion of solar spectrum and can achieve higher photocurrents
    - $GaInP_2/GaAs$ is 1.8eV/1.4eV
  - Lattice constant – *a* (Å)
  - Charge carrier mobilities – μ (cm^2/V-s)

$In_xGa_{1-x}N$

$In_{.29}Ga_{.71}N$ $In_{.33}Ga_{.67}N$ $In_{.40}Ga_{.60}N$ $In_{.41}Ga_{.59}N$ $In_{.48}Ga_{.52}N$

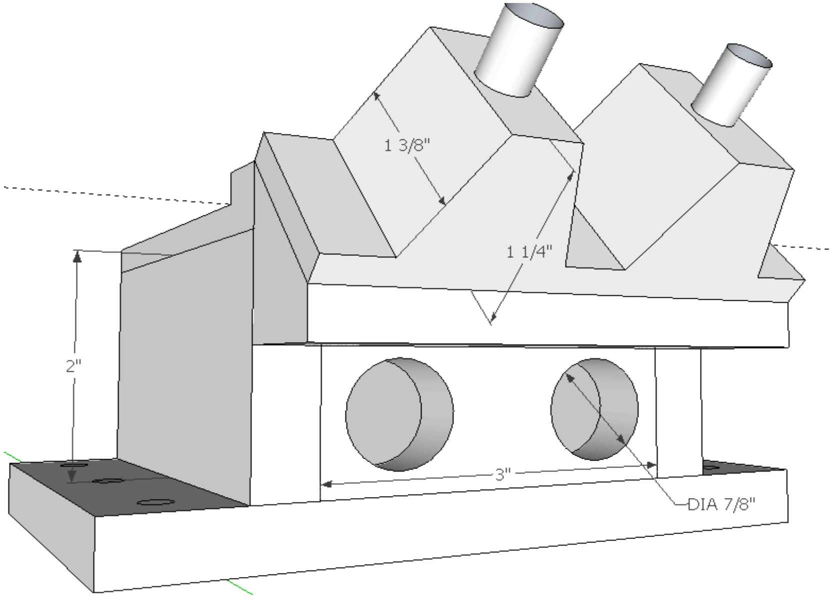


Technical Accomplishments – Photoreactor for On-sun Testing

Photoreactor design, fabrication, and testing

Developed photoreactor for outdoor testing to evaluate durability and efficiency under real-world conditions

- Made from PMMA for optimal chemical resistance and optical transparency
- Mounted on a solar tracker at NREL's Solar Radiation Research Laboratory
- Real-time solar spectral and intensity data used to evaluate solar-to-hydrogen efficiency



Gases collected by inverted pipettes
Pressures equalized by leveling funnel

Technical Accomplishments – Springer Brief Publication

Standardization of PEC result reporting

- Motivated by inaccurate efficiency reporting throughout PEC literature
- Material that didn't make it into abbreviated Journal of Materials Research (JMR) review paper turned into a Springer short book
- Photoelectrochemical Water Splitting – Standards, Experimental Methods, and Protocols
- Editors:
  - Zhebo Chen – Stanford
  - Huyen Dinh – NREL
  - Eric Miller – DOE

REVIEW

This section of Journal of Materials Research is reserved for papers that are reviews of literature in a given area.

Accelerating materials development for photoelectrochemical hydrogen production: Standards for methods, definitions, and reporting protocols

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Original JMR paper cited over 100 times

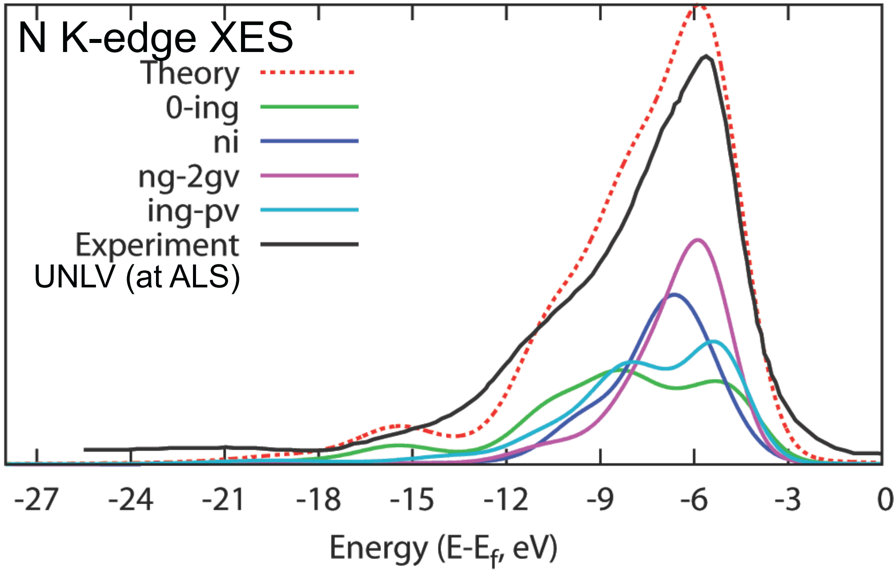
http://www2.eere.energy.gov/hydrogenandfuelcells/pec_standards_review.html

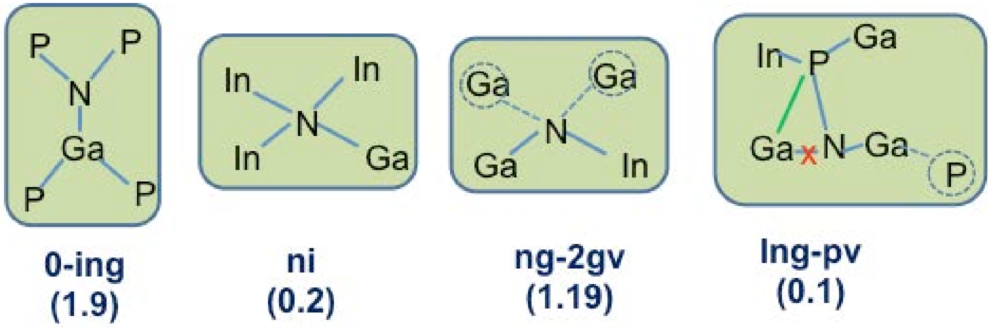
Technical Accomplishments – Surface Validation Theoretical Modeling

Theory and modeling used to interpret and understand surface spectroscopy results

- NREL and UNLV collaborate with the Quantum Simulations (Ogitsu) group at Lawrence Livermore National Lab to help interpret and complement experiments
    - One highlight – use calculated N K-edge x-ray emission spectra of various nitride incorporation environments in $GaInP_2$ to deconvolute UNLV measured spectra of N_2^+ treated $GaInP_2$ materials

See next talk PD058 for details of theory work at LLNL





Collaborations

Partners (extensive collaboration with all)

- University of Nevada Las Vegas
  - As-grown, nitride treated, and PEC tested $GaInP_2$ samples sent to Heske group for X-ray spectroscopic characterization both at UNLV and the Advance Light Source to identify corrosion intermediates and products and uncover chemistry of protected surfaces
  - Key partner in surface validation project
- 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)
- 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 high surface area transparent conductive oxides and quantum confined nanostructured transition metal dichalcogenides (PD033)
  - Key partner in PEC standardization efforts
- University of Texas-Arlington
  - Professor Muhammad Huda for PEC materials theory and modeling (PD052)
- MVSystems, Inc. (Industry)
  - Program production solicitation
  - We provide efficiency and durability characterization of a-SiC:H obtained from our collaborator (PD053)

Collaborations

Partners (extensive collaboration with all)

- Los Alamos National Laboratory
  - Todd Williamson synthesizes InGaN samples (PD097)
- Colorado School of Mines
  - Graduate, postdoc and assistant professor research associates; electron microscopy and XPS user facilities; sample exchange
- University of Colorado-Boulder
  - Host two NSF-graduate research fellow associates
- University of Louisville
  - Sunkara group- ALD of TiO_2 on $GaInP_2$
  - Several graduate students visited to learn PEC characterization techniques
- University of Oregon
  - Boettcher group- Joint InGaN PEC characterizations

Proposed Future Work

- **Work with surface validation team**
  - Optimize nitrogen ion treatment and understand protective mechanism through spectroscopic observations and theoretical modeling by our surface validation team partners
- **Expand nitrogen ion implantation treatment**
  - Once optimized, apply to $GaInP_2$/GaAs tandem surfaces and test at short-circuit until failure and compare against 1000-hour near-term goal (key milestone)
  - Apply anti-corrosion treatment to other III-V surfaces and determine if protection translates to other material sets
- **Investigate emerging III-V alloys**
  - Variable band gap $In_xGa_{1-x}N$ and $GaAs_{1-x}Bi_x$ systems
  - Develop tandem configurations that will provide potential difference necessary for photoelectrolysis while maximizing current in order to meet future DOE efficiency targets
- **Photoreactor testing under on-sun conditions**
  - Evaluate efficiency and durability of III-V materials in photoreactors mounted on solar trackers that use intrinsic (~10x) concentration
  - Response to diurnal and intermittent (clouds) light cycling
- **Monitor breakthrough advances in III-V synthesis**
  - Develop economic models (with NREL analysts) to determine if cutting-edge techniques such as epitaxial lift off can provide high volume III-V fabrication at the cost reductions necessary to achieve economical PEC hydrogen production (Alta Devices, Microlink Devices)

Project Summary

Relevance:	Spearheading research in high-efficiency materials in order to meet DOE metrics and objectives for solar-hydrogen generation
Approach:	Focus on high-efficiency III-V crystalline semiconductor systems, an NREL core competency: investigation of new materials and configurations as well as stabilization of $GaInP_2$ surface
Technical Accomplishments:	Reproduced protective treatment for $GaInP_2$ surfaces and are optimizing it with assistance from UNLV; progress in understanding nitride incorporation and its role in mitigating corrosion through spectroscopy and theory partnership; characterized new III-V material $GaAs_{1-x}Bi_x$ with a potential for higher photocurrents; constructed a prototype photoreactor for mounting on a solar tracker and evaluating PEC devices under natural sunlight; Springer brief PEC standards publication
Collaborations:	Several ongoing, active collaborations with synthesis, modeling, and characterization groups
Proposed Future Work:	Optimize nitrogen ion implantation treatment with surface validation partners; apply anti-corrosion treatment to other III-V's and tandem system – test to failure at short-circuit and compare against 1000-hr benchmark; investigate emerging III-V materials with potential for higher efficiencies; photoreactor for III-V efficiency and stability evaluation under concentrated on-sun conditions; III-V economics at scale

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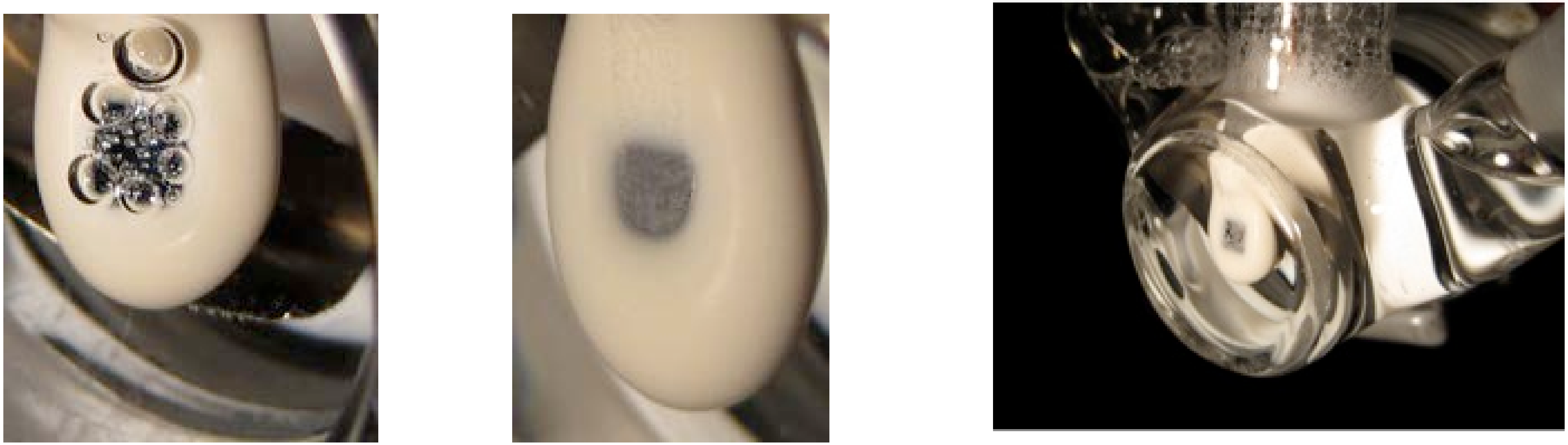
- Arrelaine Dameron – NREL
- All of our amazing collaborators noted throughout this presentation

Technical Back-Up Slides

Technical Back-Up

Logistical issues with surfactant



No surfactant

Surfactant

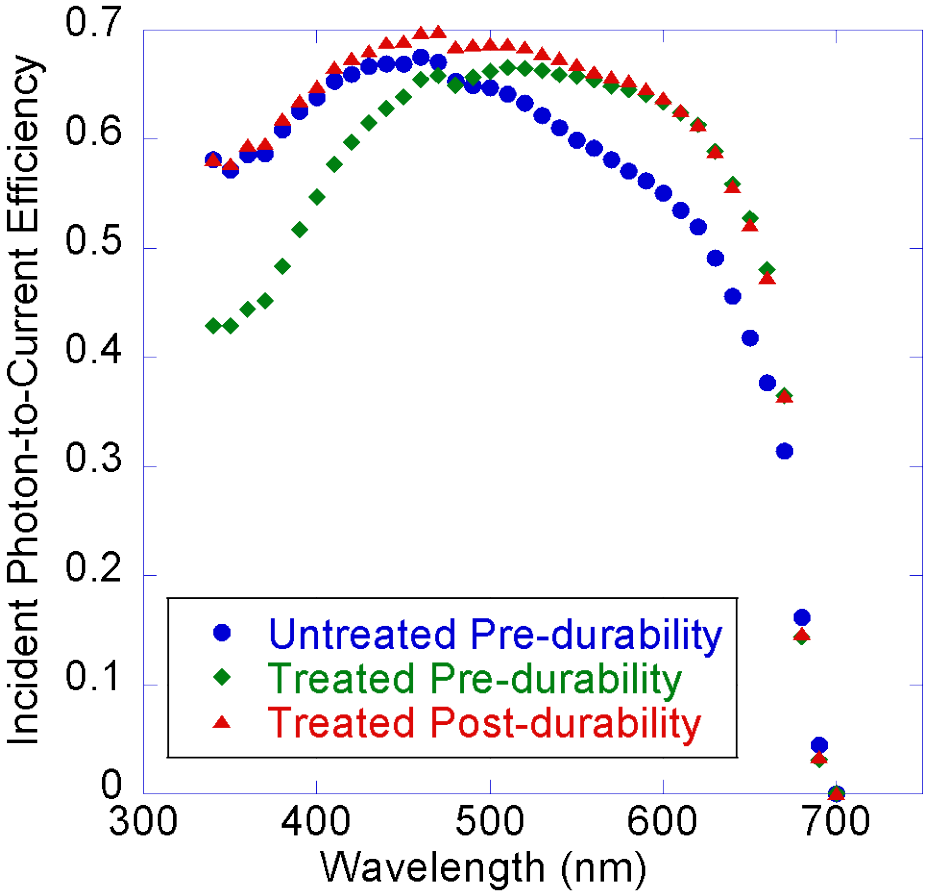
H_2 and O_2 sulfuric acid foam

Surfactant is necessary to facilitate bubble evolution but makes quantitative analysis of electrolysis products nontrivial

Semiconductor degradation is much more rapid under bubble evolution in electrolyte without surfactant

Technical Back-Up

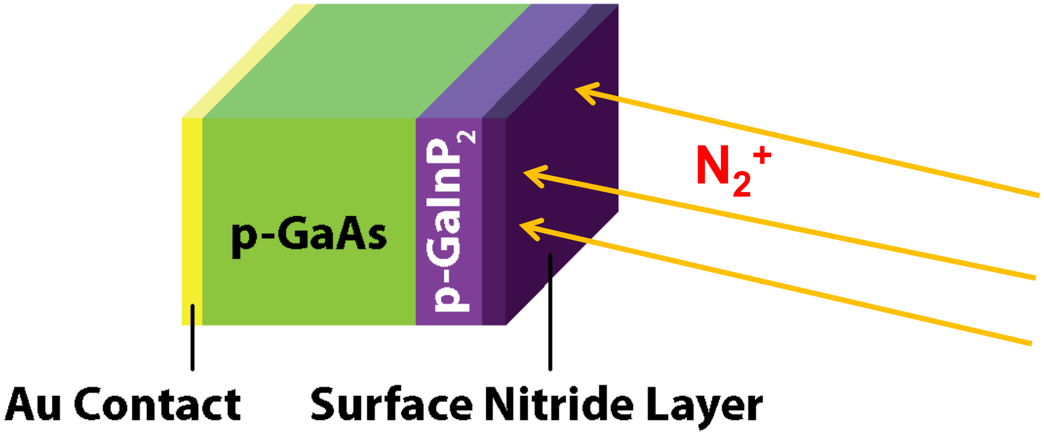
- **IPCE of treated electrode pre- and post-durability corroborate higher photocurrents after durability testing**
- **One possible explanation- hydrogen evolution could be passivating surface damage caused by ion implantation leading to improved IPCE at higher energies.**



IPCE conditions:
3M H_2SO_4 with fluorosurfactant
-0.75V vs. Ag/AgCl
300W Xe lamp with 335nm long-pass filter
Light chopped at 0.2 Hz

Technical Back-Up

- **Surface nitridation conditions**



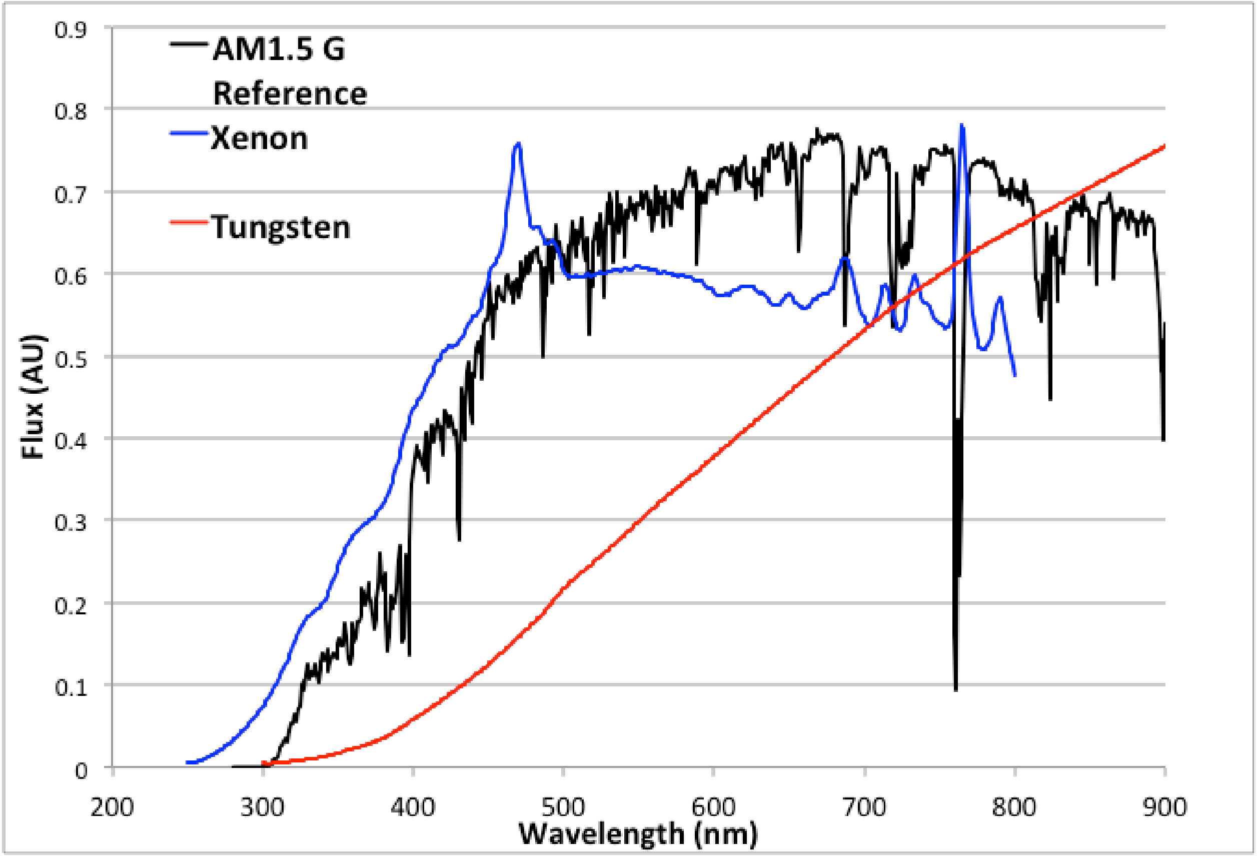
3 cm Ion Tech gridded source.
Angle: 55 degrees
Distance: 8 inches.
Pressure: 7.0 E-4 torr (Nitrogen)
Filament current (Source) 3.21A
Discharge current 0.22A
Discharge voltage 55V
Beam current 12mA
Beam voltage 550V
Accelerator current 2mA
Accelerator voltage 100V
Neutralizer current 10mA
Filament current (neutralizer) 2.94V

Samples treated for 30 seconds

Technical Back-Up

Spectral mismatch simulating AM1.5G using laboratory light sources

- **Sun: 5800K blackbody radiator**
    - Absorption bands due to atmospheric constituents
- **Tungsten: 3200K blackbody**
- **Xe: 6000K-with emission lines**



Scaled fluxes for comparison

Multijunction absorber device STH efficiencies measured under simulated light sources need to be validated under actual solar conditions

Technical Back-Up

Pretty good match of outdoor spectrum with reference spectrum
Variation due to altitude, aerosol optical depth