NREL
NATIONAL RENEWABLE ENERGY LABORATORY

Semiconductor Materials for Photoelectrolysis

2012 Hydrogen & Fuel Cells Program Review

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May 16th, 2012

Project ID: PD035

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

NREL is a national laboratory of the U.S. Department of Energy, Office of Energy Efficiency and Renewable Energy, operated by the Alliance for Sustainable Energy, LLC.

Overview

Timeline

- Project start date: 2004
- Project end date: 9/2012*
- Percent complete: 90%

Budget

- Total project funding
  - DOE share: $9M
- Funding received in FY11: $1290k**
- Planned funding for FY12: $1100k**

* Project continuation and direction determined annually by DOE

** Includes UNLV, SU and UTA 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 Colorado
  - University of Louisville
  - University of Hawaii
  - Stanford University (SU)
  - University of Texas-Arlington (UTA)
  - Program production solicitation
    - MVSystems, Inc.
  - Small Business Innovation Research
    - Synkera Technologies, Inc.

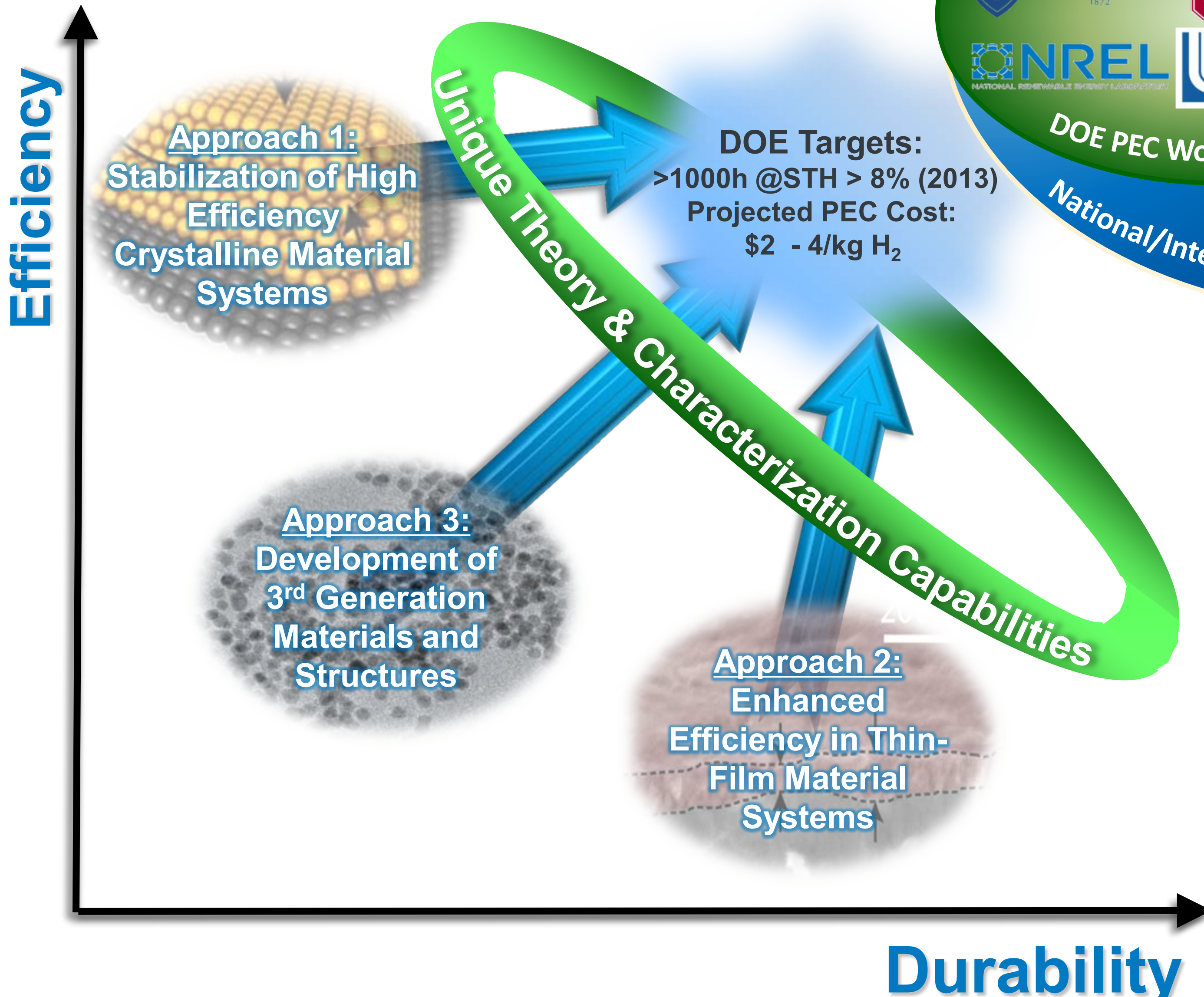
Relevance

- 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 this past year has been to work with state-of-the-art materials that **meet DOE's near-term efficiency targets and investigate surface treatments that promote durability**.

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

Approach



DOE PEC Working Group

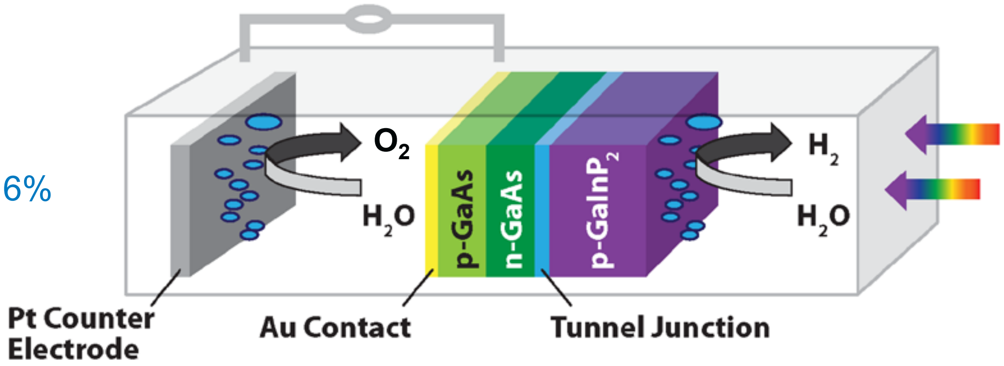
National/International Collaborations

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

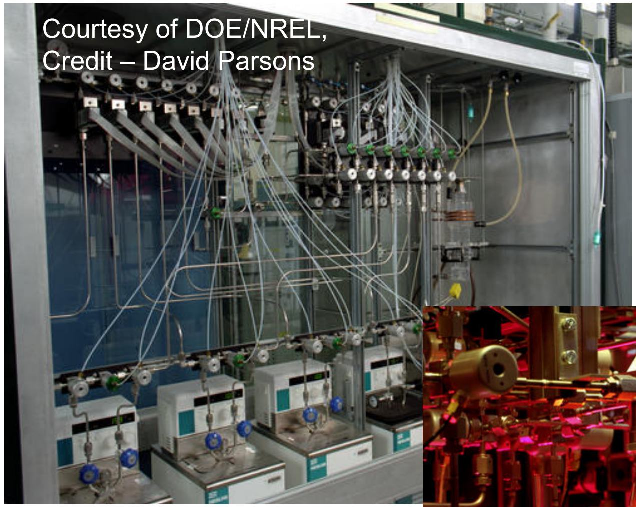
Approach: Engineering Known Materials

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

- **Unmatched Efficiency**
  - Only demonstrated system that exceeds unbiased 10% solar-to-hydrogen target
    - 12.4% with Pt-black counter electrode, >16% with RuO_2 CE
  - Metal organic chemical vapor deposition (MOCVD) synthesis
    - Synthesis by NREL's III-V team



- **Focus: Address instability**
  - Ideal system for observing and modeling corrosion
  - Can tolerate efficiency losses due to protective treatment and still meet 10% target



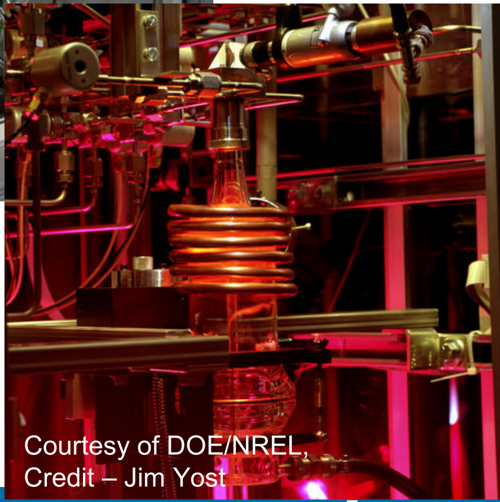
MOCVD reactor

Nitride-based passivation treatments

- **Dilute nitrides (1% N in GaPN, GaInPN) have improved stability in III-V PEC systems**
  - Nitride on surface offers protection
  - Nitride in bulk lowers conversion efficiency
  - More localized bands of nitrogen p-orbitals are responsible for stability– increases bulk modulus
    - Muhammad Huda: Theory collaborator at UT-Arlington

JPCB, 2006, **110**, p.25297.

JES, 2008, **155**:9, p.B903.



Approach: Surface Validation Team

Partner with specialists that have unique expertise and resources

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

- **Heske group at UNLV** **(PD051)**
  - 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

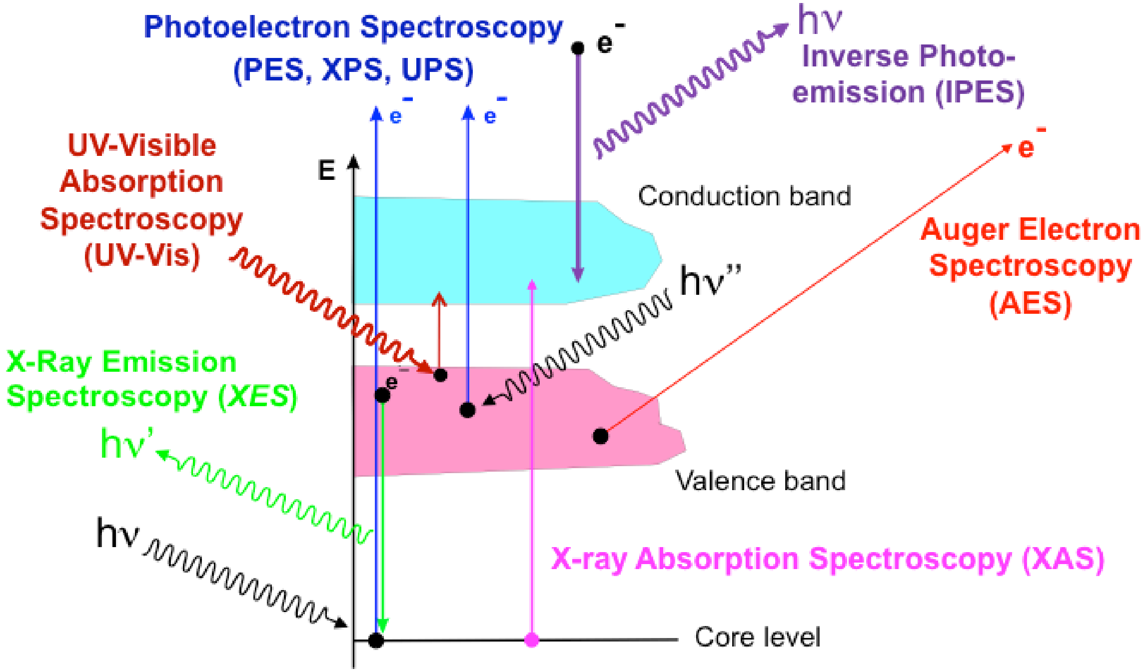


Diagram courtesy of Clemens Heske

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

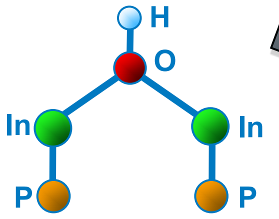
1. Study PEC corrosion in III-V's, the simplest (model) system to uncover corrosion initiation sequence and develop remediation strategy
2. Identify chemical character and mechanism of successful protective treatments
3. Apply lessons learned to other inexpensive systems (polycrystalline thin-film, amorphous)

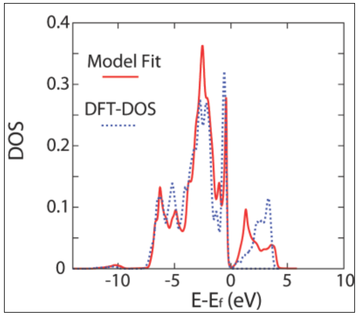
Approach: Surface Validation Team

Partner with specialists with unique expertise and resources

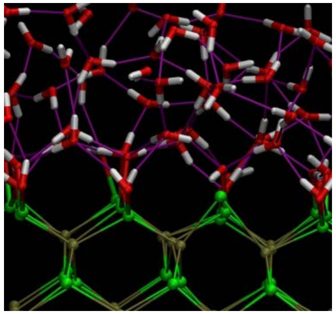
Theoretical modeling of the electronic structure of III-V ($GaInP_2$)

- **Partner with Ogitsu group at LLNL (PD058)**
  - Calculate XAS and XES spectra to correlate experimental result with surface/near surface compositions
  - Molecular dynamics simulations
  - Model surfaces for mechanistic understanding of hydrogen evolution and corrosion





Courtesy of Woon Ih Choi and Brandon Wood (LLNL)



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
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Approach – Milestones

Milestone	Due Date	Status
Complete operational endurance measurements on $GaInP_2$ semiconductor electrodes that have had nitride based surface passivation treatments and determine the durability benchmarked against the 100-hour operational lifetime at 10% efficiency target.	05/12	Completed
Complete design for cells that allow for outdoor measurements under real-solar conditions and permit product gas capture for efficiency benchmarking.	07/12	60%
Evaluate dual photoelectrode system performance under real-solar conditions and identify a promising coupling that could be optimized to maximize efficiency and durability at low cost.	09/12	40%
Complete advanced spectroscopic studies with UNLV on III-V materials systems as part of the collaborative "Surface Validation Study". Use results to determine the effectiveness of corrosion mitigation schemes for achieving >100 hour operational durability in III-V materials systems capable of >10% STH conversion efficiency	09/12	60%

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

Technical Accomplishments

Outline

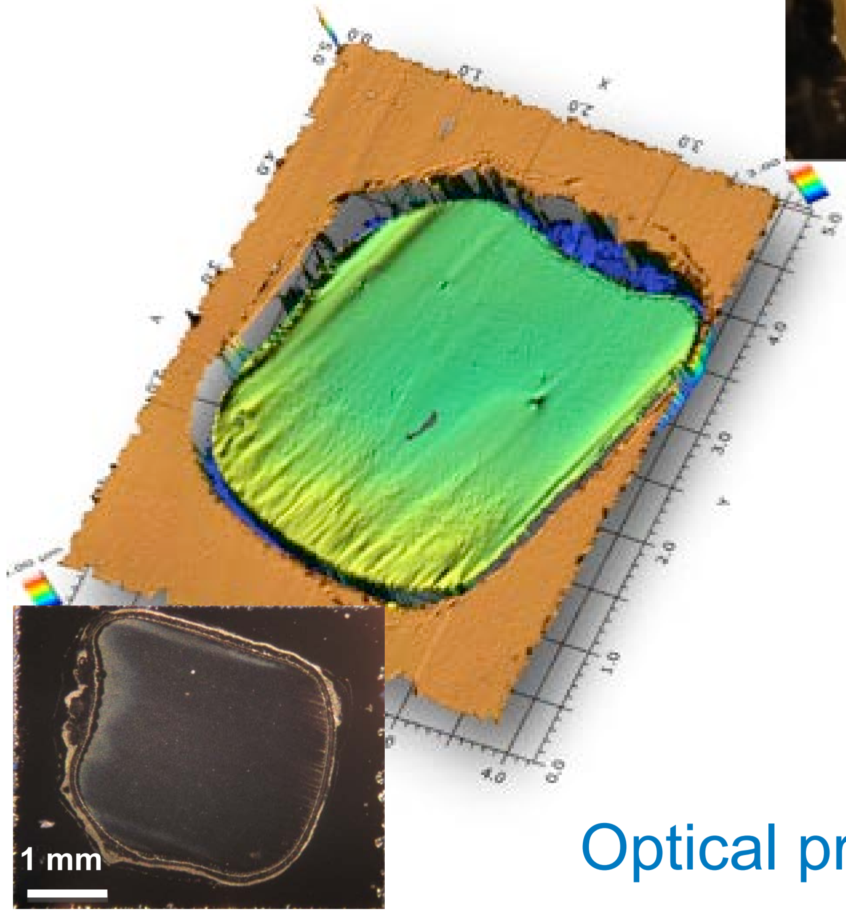
- **Designed effective protective treatment for high-efficiency III-V's**
  - Nitride passivated surface achieved over 100+ hours of undamaged operation
- **Surface validation team collaboration**
  - Spectroscopic characterization identified chemistry of protected surface (UNLV)
  - Established baseline spectra of air-excluded as-grown $GaInP_2$ samples (UNLV)
  - Theoretical modeling of X-ray spectra validated by experimental data (LLNL)
  - Molecular dynamic simulations identified precursor states of photocorrosion based on electronic structure & chemistry of local models (LLNL)
- **Progress on novel pure nitride material**
  - InGaN synthesized at Los Alamos
- **Efficiency benchmarking for multijunction absorbers**
  - Measurements under natural sunlight in collaboration with MVSystems/HNEI
- **Standardization of PEC methods and efficiency reporting**
  - Short book publication from multi-year/multi-partner collaboration

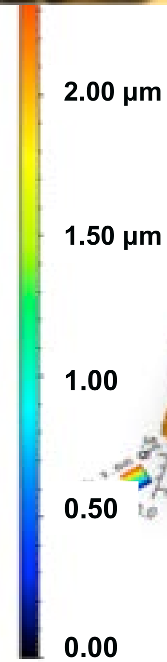
Technical Accomplishments

Nitrogen ion (N_2^+) treatment stops corrosion on high-efficiency $GaInP_2$ surfaces

No Treatment (Control)

1 µm of exposed material removed from surface after 24-hours

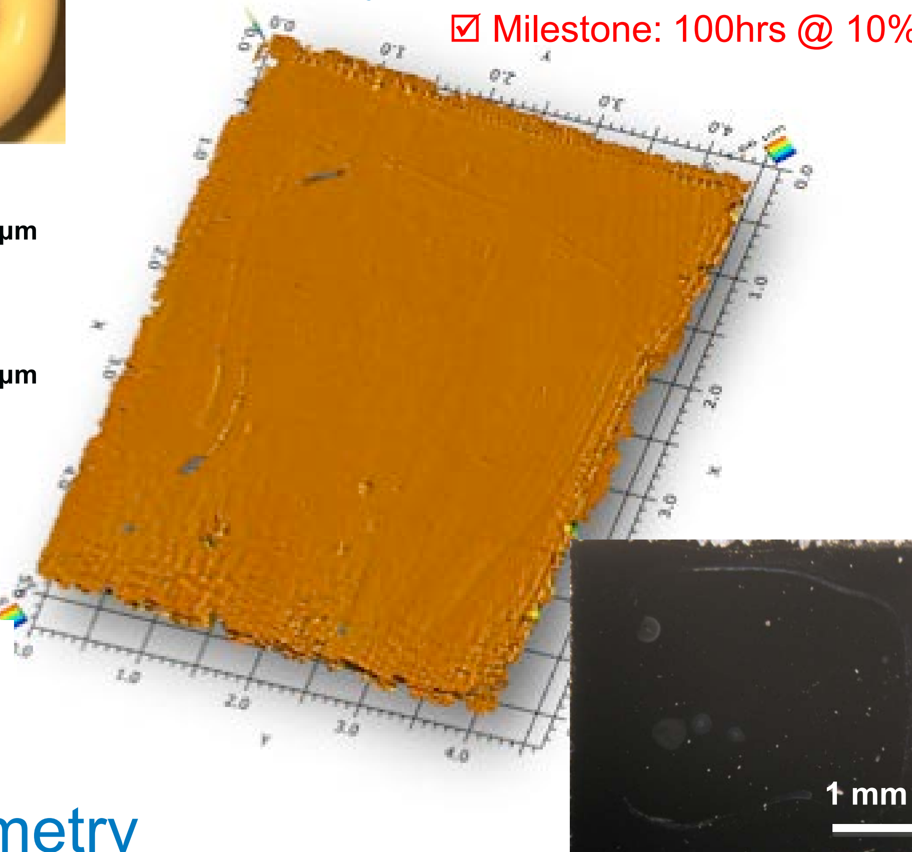




Nitrogen Ion Bombardment

Pristine surface after 115 hours at current density equivalent to 12% STH

☑ Milestone: 100hrs @ 10%



Optical profilometry

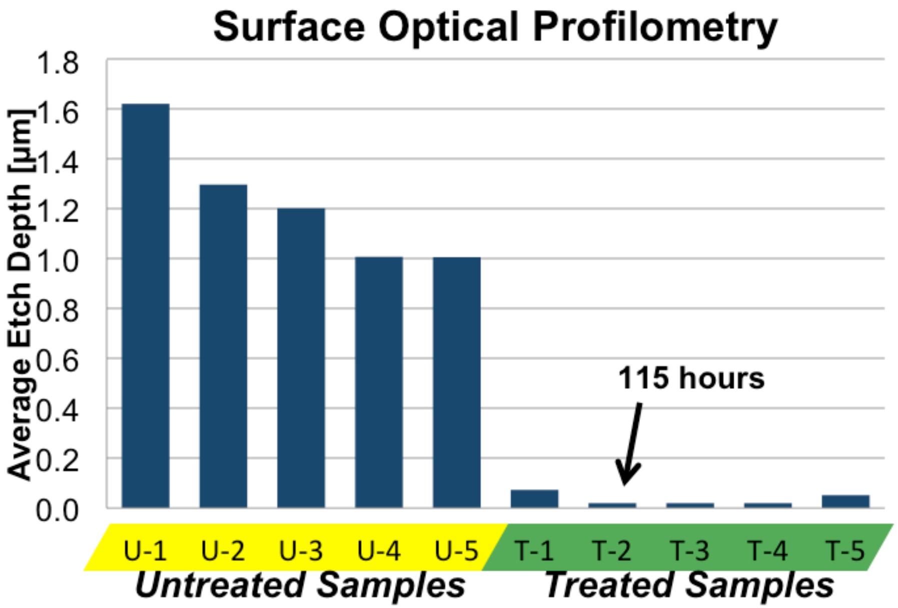
Durability Conditions: 3M H_2SO_4 with Zonyl, AM1.5G, -10mA/cm^2, Pt Black counter electrode

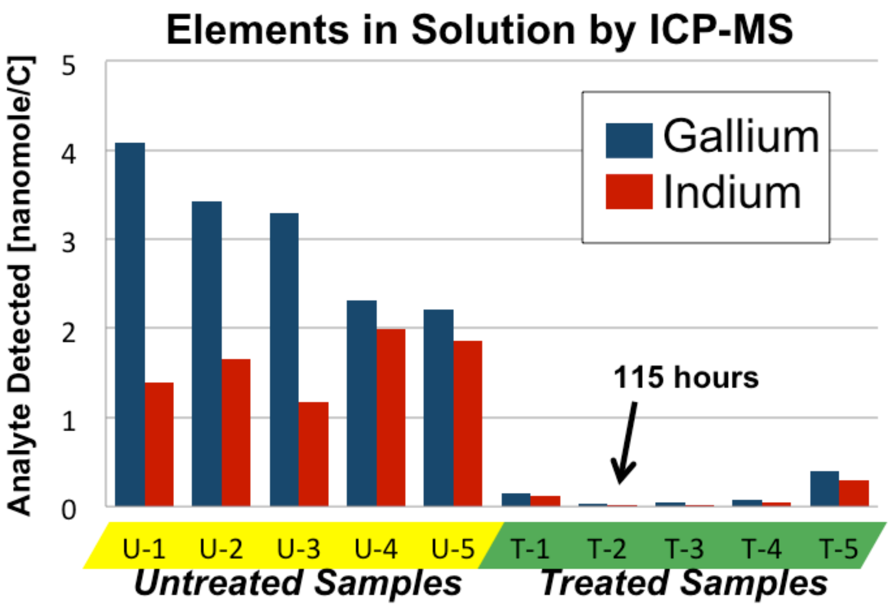
Technical Accomplishments

<u>Passivation treatment identified</u>

Durability testing demonstrates significant protection provided by of nitrogen ion (N_2^+) treatment of $GaInP_2$ surfaces; nominal reduction in photoconversion efficiency

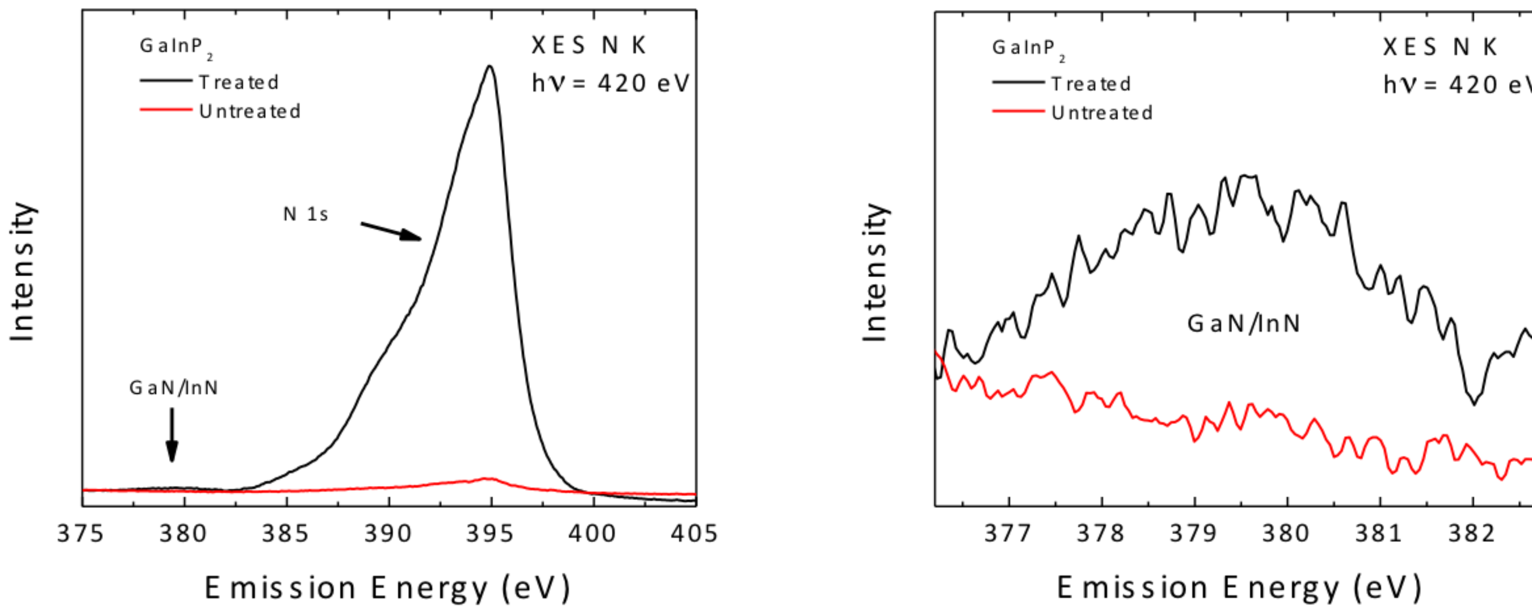
- **Durability Conditions**
  - 3M H_2SO_4 with fluorosurfactant
  - AM1.5 G simulated light
  - -10mA/cm^2 (12.3% STH equivalent) constant current applied
  - 24-hours (or longer where noted)
- **Results**
  - Optical profilometry of surfaces
    - Untreated samples exhibited significant etching
    - Treated samples had small amounts of local etching or none at all
  - Inductively coupled plasma mass spectrometry (ICP-MS) of durability electrolytes
    - Normalized for variation in surface area, solution volume, time (charge passed)
    - Treated samples had significant reduction in Ga and In detected in solution





Technical Accomplishments

Surface Validation: Spectroscopic detection of N_2^+ ion protection mechanism– incorporated as nitride



- **X-ray Emission Spectroscopy from UNLV Collaborators (Heske group)**
  - Lawrence Berkeley National Lab– Advanced Light Source
  - Data collection by Michael Weir in March 2012
  - Analysis by Michael Weir, Lothar Weinhardt, Kyle George, Clemens Heske
- **Results: Peaks around 380 eV indicate N bond to Ga/In**
  - Incorporated as a nitride, not merely a guest molecule

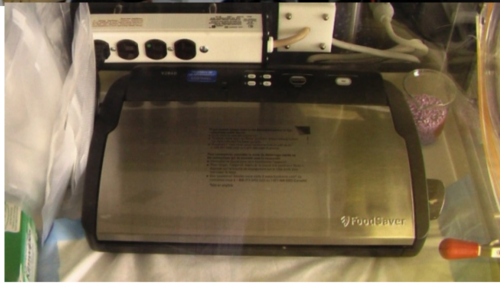
See poster PD051 for details of UNLV analysis

Technical Accomplishments

Surface Validation: Progress in establishing baseline spectra of uncorroded surfaces for comparison

- **At NREL**
  - Nitrogen purged glove bag attached to MOCVD synthesis reactor
  - 2μm thick p-$GaInP_2$ epilayer
  - Packaged under nitrogen with off-the-shelf vacuum seal device and shipped to UNLV
  - John Geisz, Waldo Olavarria from PV center

- **At UNLV (Heske group)**
  - Opened in glove box and introduced into UHV for analysis
  - X-ray Photoelectron Spectroscopy found for these samples (compared to air-exposed samples)
    - No carbon or oxygen contamination
    - Higher In/Ga ratio
    - P, In, Ga bonding have no O_x character

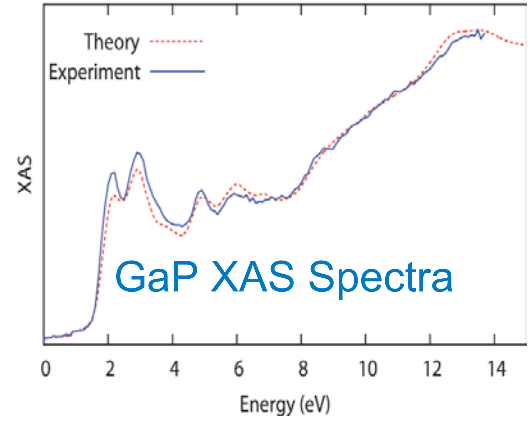


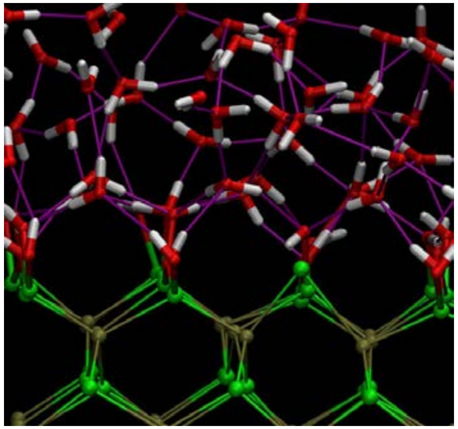
See poster PD051 for details of UNLV analysis

Technical Accomplishments

Surface Validation: Theoretical modeling (at LLNL) elucidated electronic structure at surface of $GaInP_2$

- **NREL and UNLV collaborate with the Quantum Simulations group at Lawrence Livermore National Lab to help interpret and complement experiments**
- **X-ray Absorption Spectroscopy (XAS) P-L 2,3 calculations of bulk GaP, InP, and $GaInP_2$**
  - Very good agreement between theory and experimental observations under standard conditions– good validation of complex model
  - Push complexity of models to match non-standard surfaces and conditions encountered in these systems (miscut crystal faces, bias voltage)
- **Molecular dynamic simulations**
  - Use DFT and Car-Parrinello dynamics to investigate the electronic properties of the surface and structure of the interface
  - Identify and investigate precursor states for surface photocorrosion processes
- **Examine energetics and chemistry of nitrogen incorporation**
  - Provide insight into experimental observations that dilute nitride incorporation leads to stabilization of PEC interface





Snapshot from MD simulation

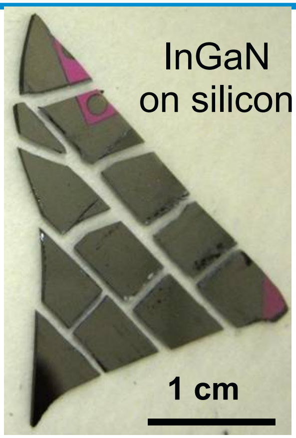
Calculations performed by B. Wood, W. Choi, and T. Ogitsu at LLNL

See poster PD058 for details of theory work at LLNL

Technical Accomplishments

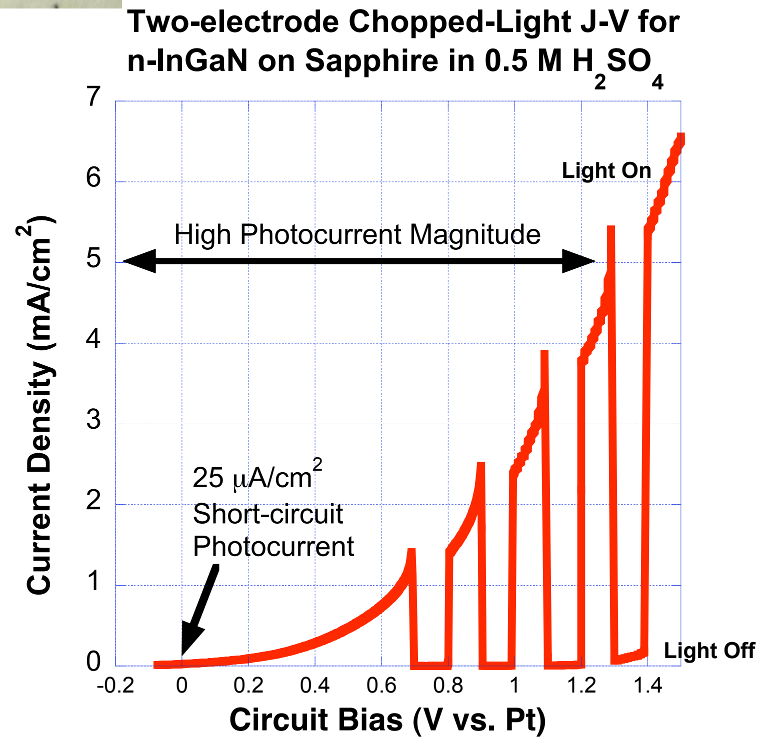
Novel III-V materials

- **Pure nitride $In_xGa_{1-x}N$ has potential to be both stable and efficient**
  - Energetic N-atom/molecular beam epitaxy synthesis
  - Full range of band gaps from 0.7 eV (InN) to 3.4 eV (GaN)
  - Either p- or n-type doping
  - New material developments
    - Can be synthesized on conductive silicon substrates
      - Previously only on sapphire
    - Much higher photocurrent under reverse bias
      - Several mA/cm^2 under 1-sun; previously 100's of $\mu A/cm^2$
      - High photocurrents observed on InGaN on both silicon and sapphire substrates
  - Ongoing activites
    - application of surface catalysts
    - durability assessment



Materials synthesized at Los Alamos National Lab by Todd Williamson

PEC characterizations at NREL



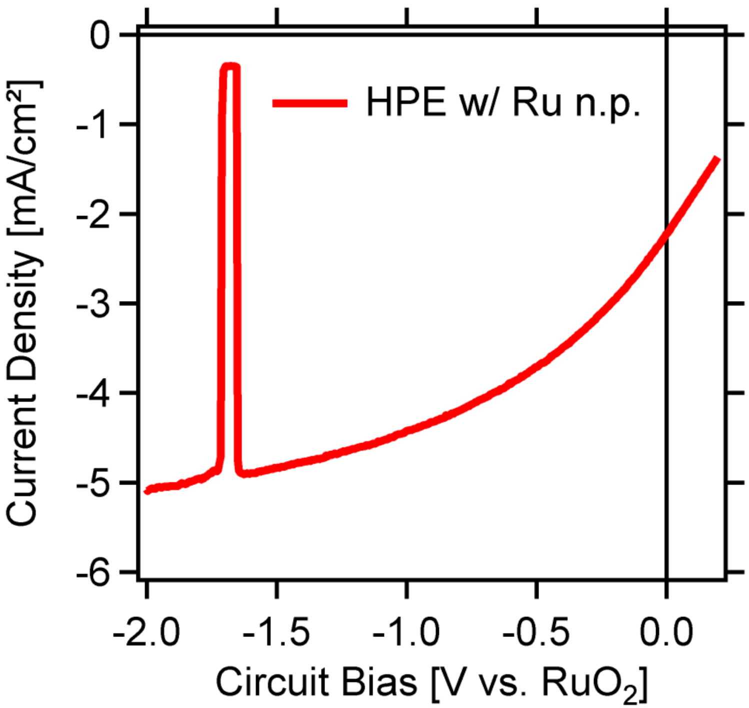
5mA/cm² is about 50% of theoretical AM1.5G max for this ~2.2 eV band gap material

Technical Accomplishments

Efficiency Benchmarking

- **Testing under real solar spectra**
  - Simulating AM1.5 G spectrum and intensity for multijunction cells is nontrivial
  - Spectral error from laboratory sources can lead to misleading solar-to-hydrogen efficiency measurements
  - NREL's Solar Radiation Research Laboratory logs insolation and spectral distribution in 1-minute intervals
    - Solar tracking instruments located adjacent to outdoor laboratory bench space
  - Outdoor testing of MVSystems Inc. a-Si/a-Si/a-SiC hybrid photoelectrodes (HPE)
    - Confirmed improved short-circuit efficiency via Ru nanoparticle surface treatment developed by HNEI
    - 2.34% Solar to Hydrogen Efficiency in pH 2
      - Total irradiance 116 mW/cm^2
      - Very good agreement with HNEI result (2.5%)
      - Difference likely due to 1-month air exposure

Outdoor testing at NREL
http://www.nrel.gov/midc/srrl_bms/



See talk PD053 for MVSystems/HNEI details & results

Technical Accomplishments

Standardization of PEC result reporting

- **Multi-year project to codify protocols and methods as well as standards for reporting PEC efficiency to permit realistic inter-laboratory comparisons**
  - 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
  - Huyen Dinh (NREL) facilitated
  - Published abbreviated version as Review paper in Journal of Materials Research in January 2010
    - Cited 41 times (as of April)
- **Contract to publish (under review) the complete document as short book**
  - Co-editors: Huyen Dinh (NREL), Eric Miller (DOE), Zhebo Chen (Stanford)
  - Incorporating feedback from national and international reviewers via sharepoint site

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

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 (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)
- 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
  - Subcontract with Professor Muhammad Huda for PEC materials theory (PD052)
- MVSystems, Inc. (Industry)
  - Program production solicitation
  - We provide efficiency and durability characterization of a-SiC:H obtained from our collaborator (PD053)

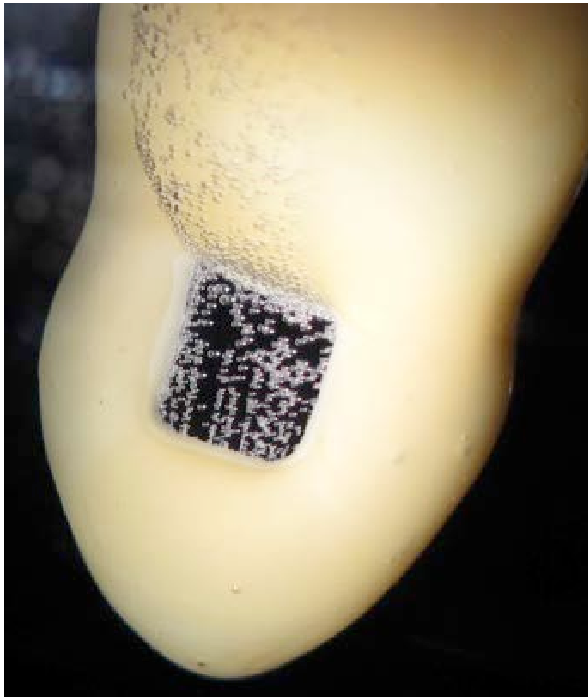
Collaborations

Partners (extensive collaboration with all)

- Colorado School of Mines
  - Graduate, postdoc and assistant professor research associates; electron microscopy and XPS user facilities; sample exchange
- University of Colorado-Boulder
  - Host graduate research associate
  - ICP-MS analysis
- 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

Proposed Future Work

- **Apply nitride treatment to tandem electrodes**
  - Test at short-circuit until failure and compare against 1000-hour near-term goal
- **Work to optimize $In_xGa_{1-x}N$ material**
  - Synthesis conditions to maximize photocurrent magnitude and application of surface catalysts to improve kinetics and onset potential
  - Possible first non-tandem material to use visible light for unbiased photoelectrolysis with high-efficiency
- **Develop cells for outdoor testing for durability and efficiency under real-world conditions**
  - Response to diurnal and intermittent (clouds) light cycling
- **Evaluate dual electrode configurations**
  - Stacked or side-by-side systems could have advantages over monolithic III-V
  - Higher efficiencies (photocurrents) possible with lower band gap combinations
    - Optimal combination for stacked system is 1.6eV/1.0eV; $CuGaSe_2$/Si
  - Potential for materials via low-cost synthesis routes
- **Continue to work closely surface validation team**
  - Understand corrosion in III-V and apply knowledge to more complex material systems



Project Summary

Relevance:	Pushing PEC technology forward to meet DOE metrics and objectives for solar-hydrogen generation
Approach:	Focus on III-V crystalline semiconductors: stabilization of high-efficiency systems and investigation of new materials and configurations
Technical Accomplishments:	Developed protective treatment that led to 100+ hours of durability; progress in understanding corrosion through spectroscopy and theory partnership; high photocurrents achieved in new InGaN material set; multijunction efficiency benchmarking using natural sunlight; PEC standards publication
Collaborations:	Several ongoing, active collaborations with synthesis, modeling, and characterization groups
Proposed Future Work:	Test nitride treated tandem system to failure at short-circuit and compare against 1000-hr benchmark; develop pure nitride material; efficiency and stability evaluation under actual solar conditions

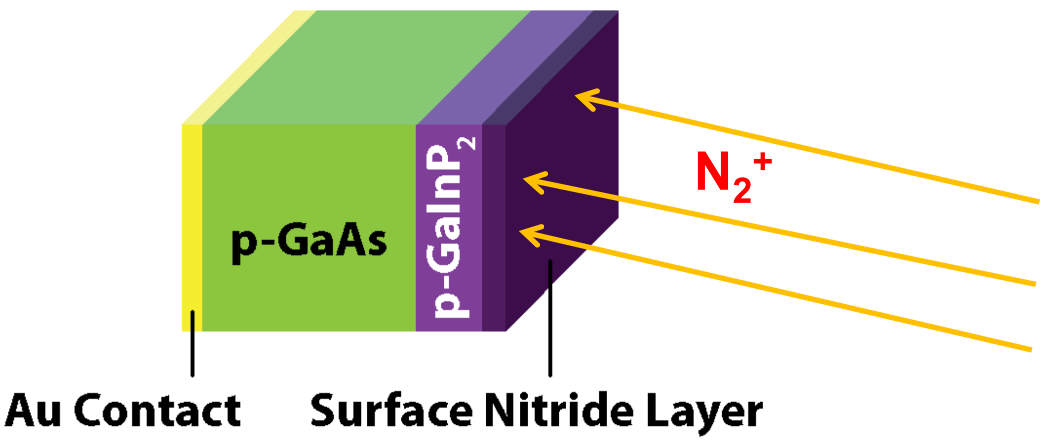
Acknowledgements

- Adam Welch – NREL/Colorado School of Mines (GS)
- James Young – NREL/University of Colorado-Boulder (GS)
- Heli Wang – NREL
- Huyen Dinh – NREL
- Avery E. Lindeman – (intern) Harvard University (UG)
  - $GaInP_2$ ion bombardment characterizations
- All of our amazing collaborators noted throughout this presentation

Technical Back-Up Slides

Technical Back-Up

- **Surface nitridation conditions**

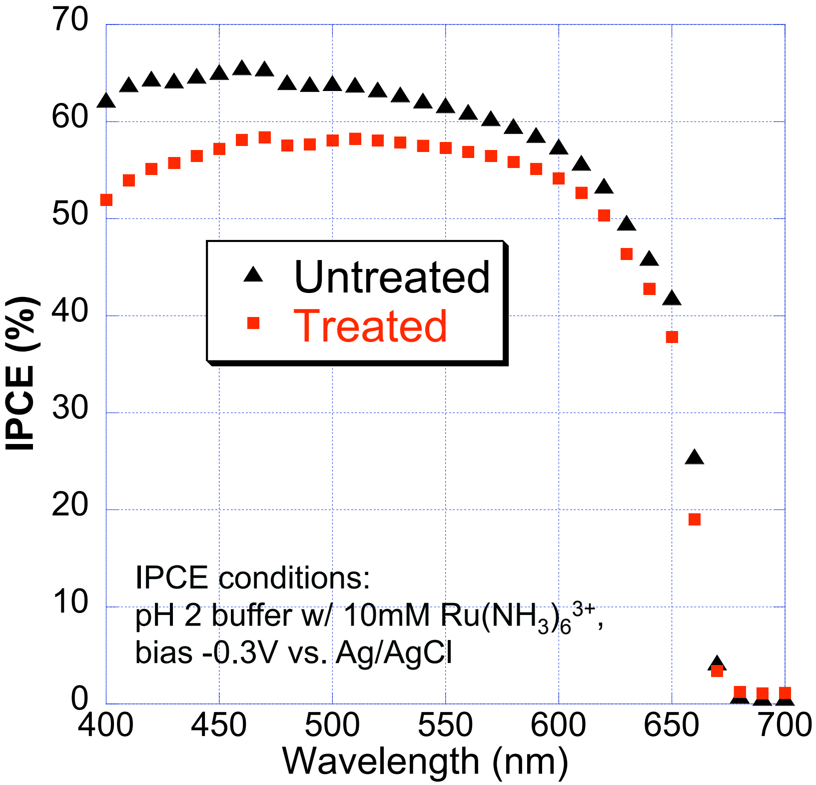


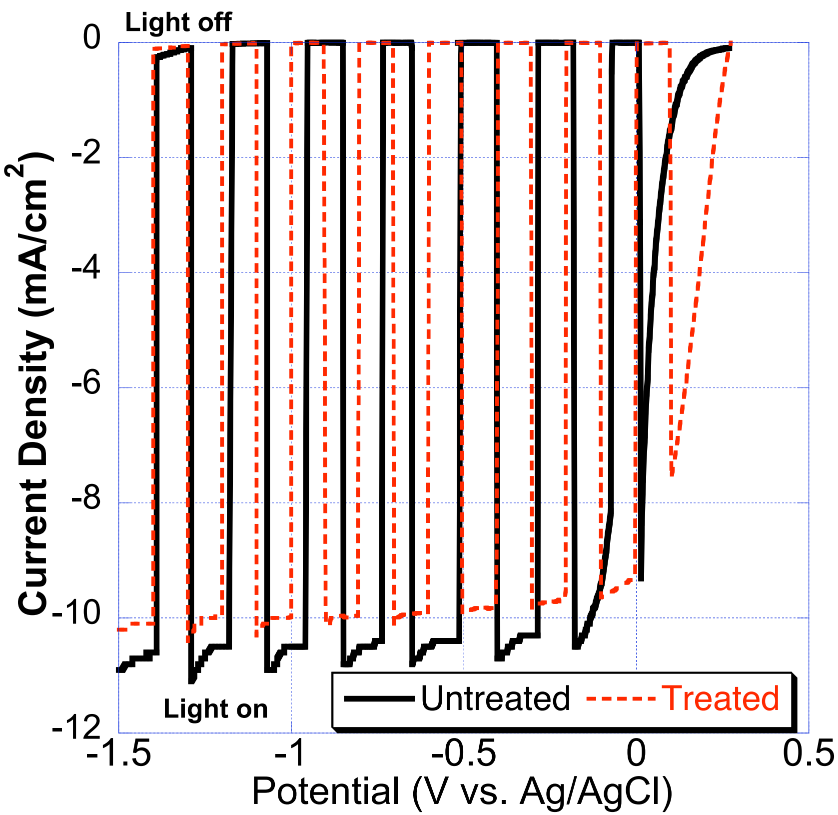
3 cm Ion Tech gridded source.
Angle: 55 degrees
Distance: 8 inches.
Pressure: 2.4e-4 torr (Nitrogen)
Filament current (Source) 3.05A
Discharge current 0.33A
Discharge voltage 55V
Beam current 13mA
Beam voltage 550V
Accelerator current 8mA
Accelerator voltage 100V
Neutralizer current 6mA
Filament current (neutralizer) 2.38V

Samples treated for 45 seconds

Technical Back-Up

Nitride treatment leads to moderate loss in conversion efficiency





0.5M H_2SO_4, tungsten light source calibrated to AM1.5 with $GaInP_2$ reference cell

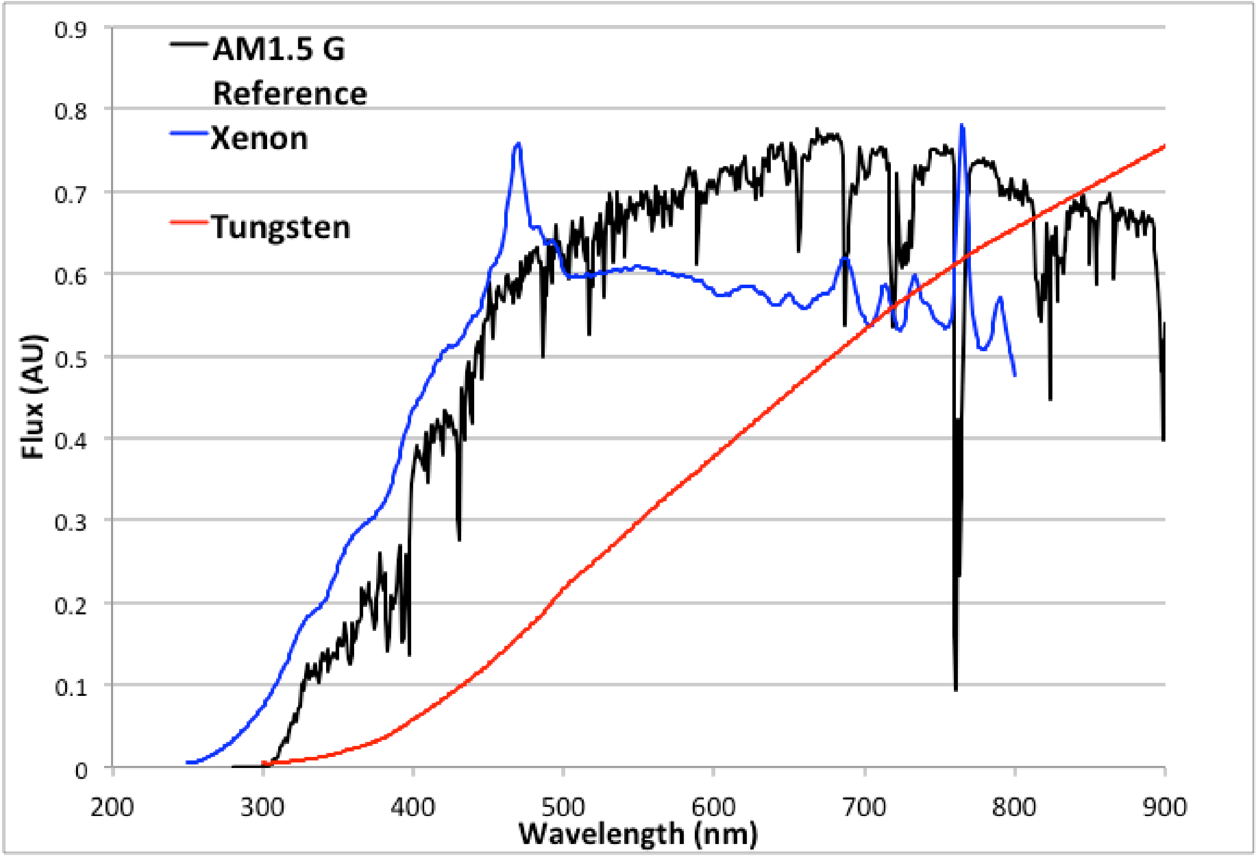
Small difference between incident photon-to-current efficiency (IPCE) for untreated and N_2^+ treated electrodes: greatest deviation at high energy wavelengths where absorption occurs closer to the surface

Slightly lower photocurrent magnitude on nitride treated electrodes under broadband illumination (AM1.5 G)

Technical Back-Up

Spectral mismatch simulating AM1.5G using laboratory light sources

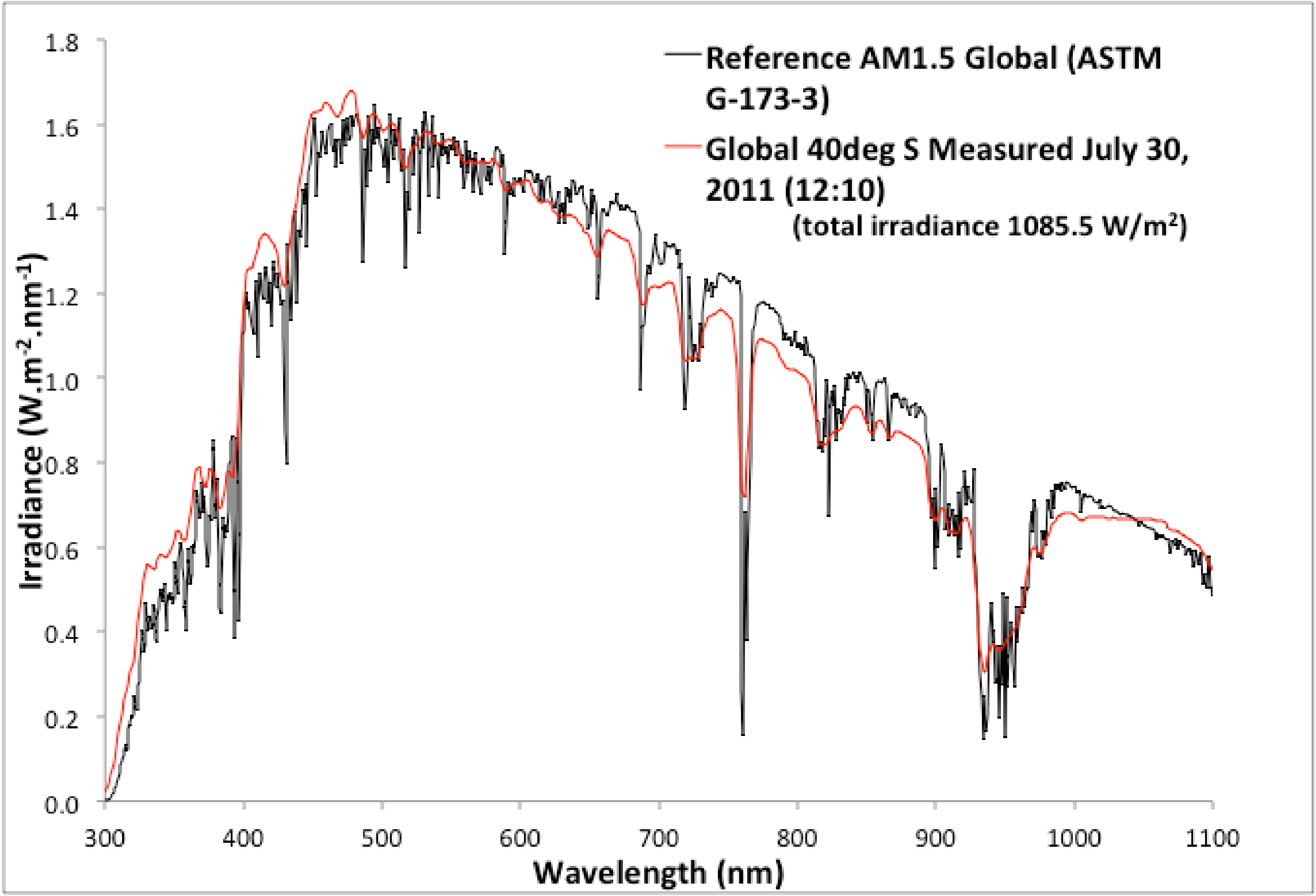
- **Sun: 5800K blackbody radiator**
  - Absorption bands due to atmospheric constituents
- **Tungsten: 3200K blackbody**
- **Xe: 6000K-with emission lines**



Scaled fluxes for comparison

Technical Back-Up

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



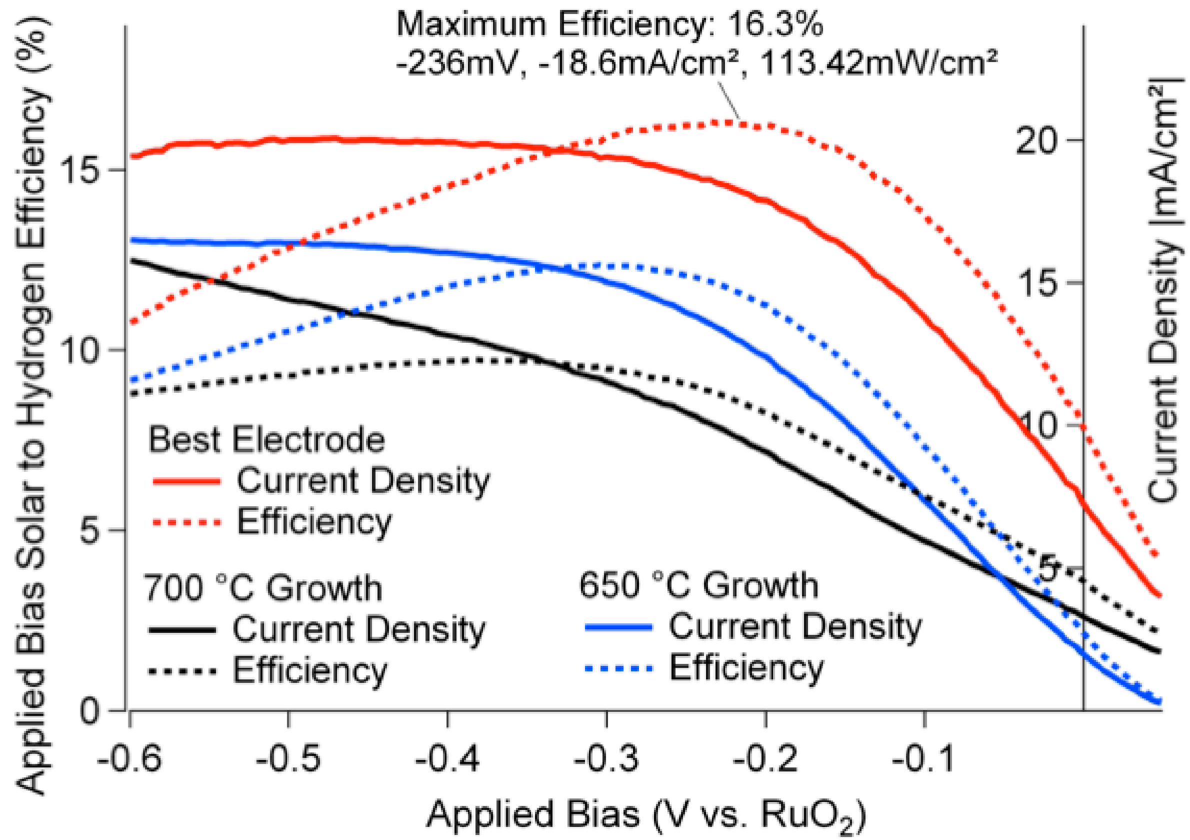
Technical Back-Up

Outdoor Tandem Cell Efficiency

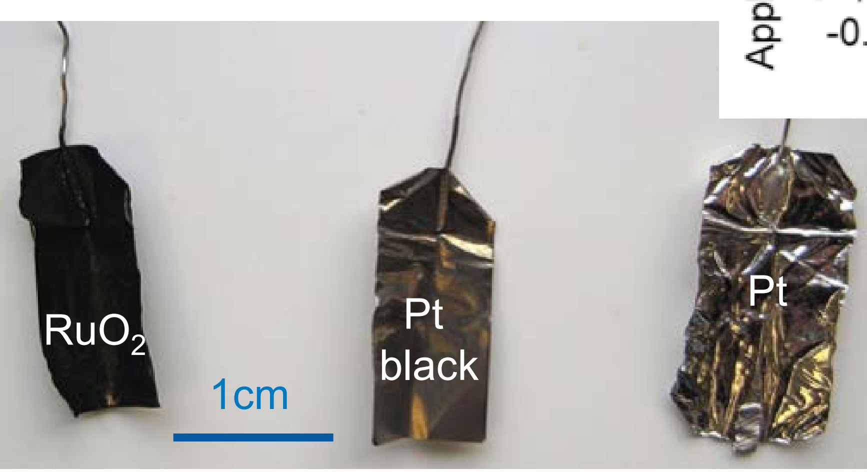
- **$GaInP_2$/GaAs Tandem Cells**

Khaselev, Turner *Science* ***208,*** 1998

  - 12.4% Solar to hydrogen efficiency (STH) with Pt-black counter electrode
  - New measurements under natural sunlight
    - More active RuO_2 improves efficiency
    - Over 16% (biased) efficiency using total irradiance



Outdoor Measurements 03/01/2011



Two different batches of $GaInP_2$/GaAs tandem cell electrodes synthesized at different temperatures; data is average of about 12 electrodes from each set

$$\textbf{Efficiency} = \frac{\textbf{(chemical potential – circuit bias) * (rate)}}{\textbf{Light intensity}}$$

$$= \frac{(1.23-0.236)\text{V} * 18.6\text{mA/cm}^2}{113.42\text{mW/cm}^2} = \textbf{16.3\% solar-to-hydrogen}$$