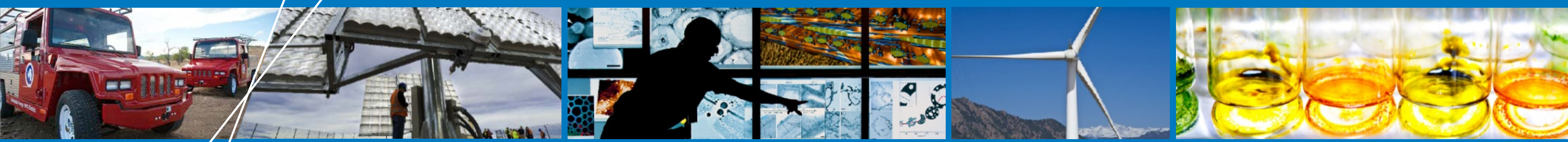
High-Efficiency Tandem Absorbers for Economical Solar Hydrogen Production



2016 U.S. DOE Hydrogen & Fuel Cells Program Review

Todd G. Deutsch

June 8th, 2016

Project ID: PD115

Overview

Timeline and Budget

- **Project start date: 10/1/14**
- **Project end date: 9/30/17**
- **Total project budget: $3M**
  - Total recipient share: $0
  - Total federal share: $3M
  - Total DOE funds spent*: $1.5M**

* As of 3/31/16

** Includes UNLV, LLNL, LANL, UH support

Barriers

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

Partners

- **Interactions/collaborations**
  - University of Nevada Las Vegas
  - Lawrence Livermore National Lab
  - University of Hawaii
  - Los Alamos National Laboratory
  - Stanford University
  - Colorado School of Mines
  - University of Colorado-Boulder
  - University of Louisville
  - University of Toledo
  - Denmark Technical University
  - JCAP-North

Relevance

Objectives

- Long-Term: Develop highly-efficient, durable material that can operate under 10-15x (or higher) solar concentration and generate renewable hydrogen for <$2/kg from photoelectrochemical (PEC) water splitting
- Current year:
    - Push boundaries on achievable semiconductor photoelectrochemical solar-to-hydrogen (STH) efficiencies
    - Benchmarking: STH efficiencies for multijunction (tandem) PEC devices
    - Continue development of stabilizing surface modifications viable at high current densities

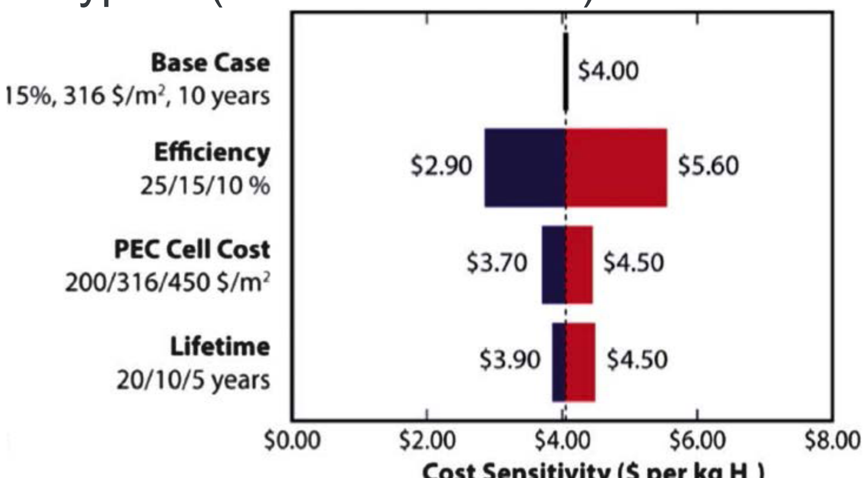
Relevance

DOE EERE Multi-Year Research, Development, and Demonstration Plan

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]	\$/m^2	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 m^2	3.3E-7	1.2E-6	1.6E-6	2.0E-6

Technoeconomic analysis for a type 4 (10x concentrator) PEC reactor



Pinaud et al. *Energy Environ. Sci.* **6**, 1983 (2013)

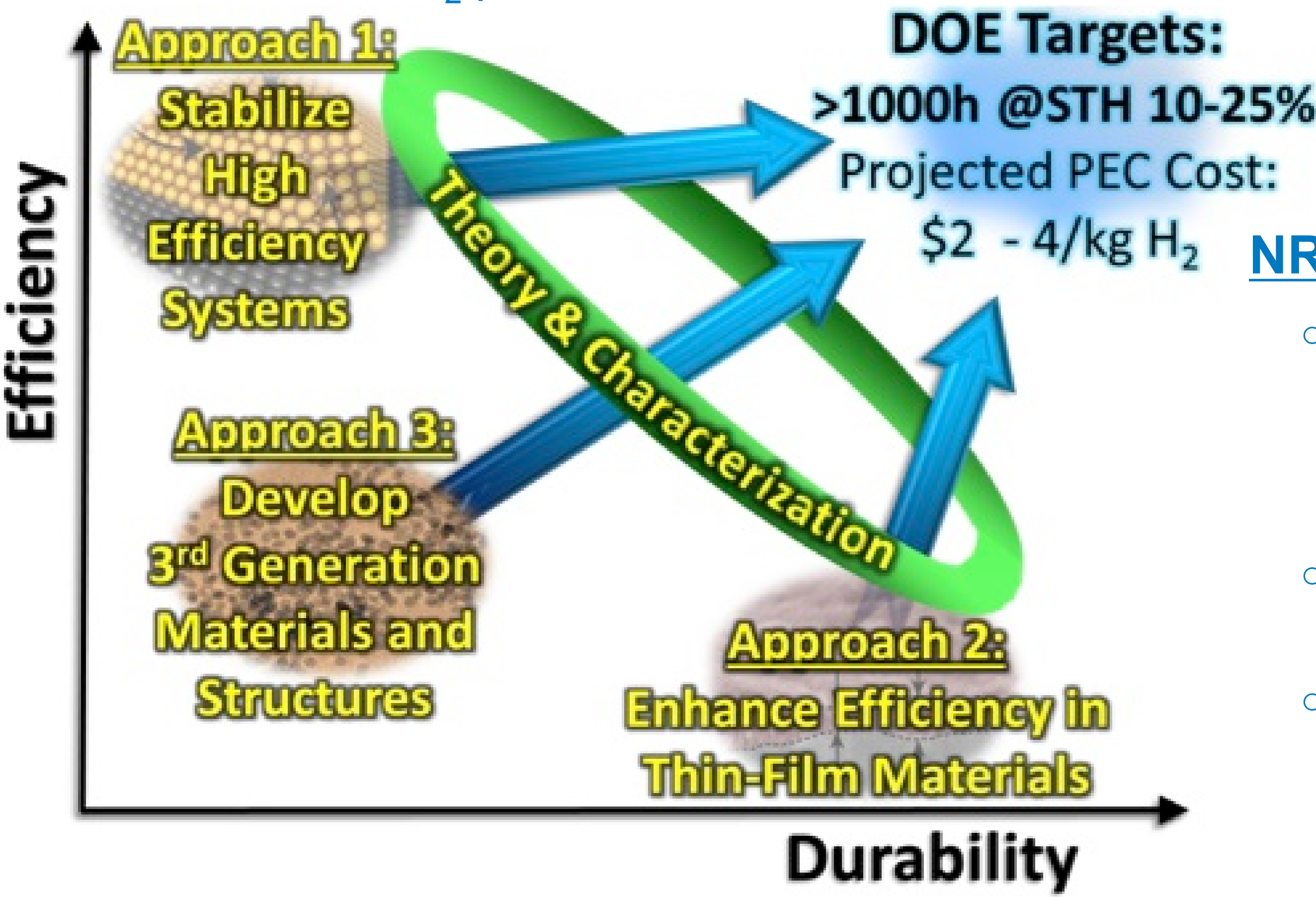
Project Guiding Principles

- Primary focus is on efficiency, the largest lever to reduce H_2 costs according to technoeconomic analysis
- Scalability is primary selection criterion, more important than earth abundance
- Durability is not an intractable issue
- Absorber cost can be addressed through engineering

Approach

EERE: Applied R&D to develop cost-effective large-scale systems
NSF: Use-inspired basic research (theory, synthesis, characterization)
Emphasis on collaboration across disciplines and institutions

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



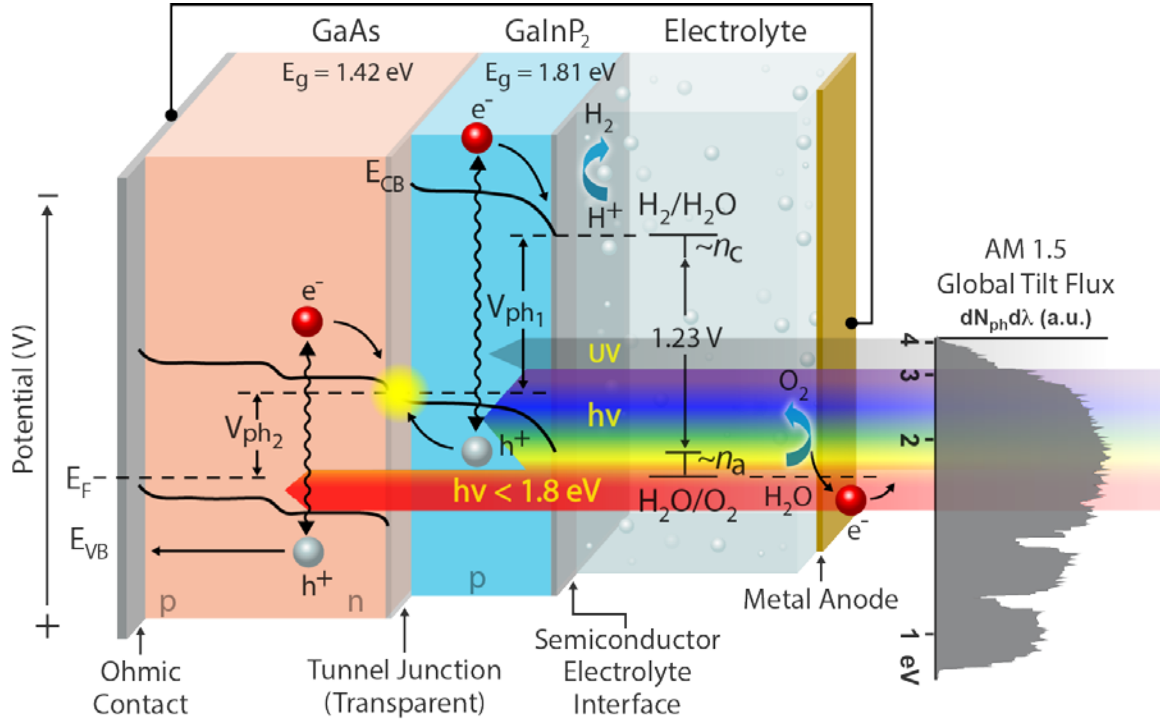
NREL-led Project Focus:

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

Approach – Project Overview

Maximize efficiency first then focus on durability via surface modifications, investigate lower-cost synthesis once material has been identified

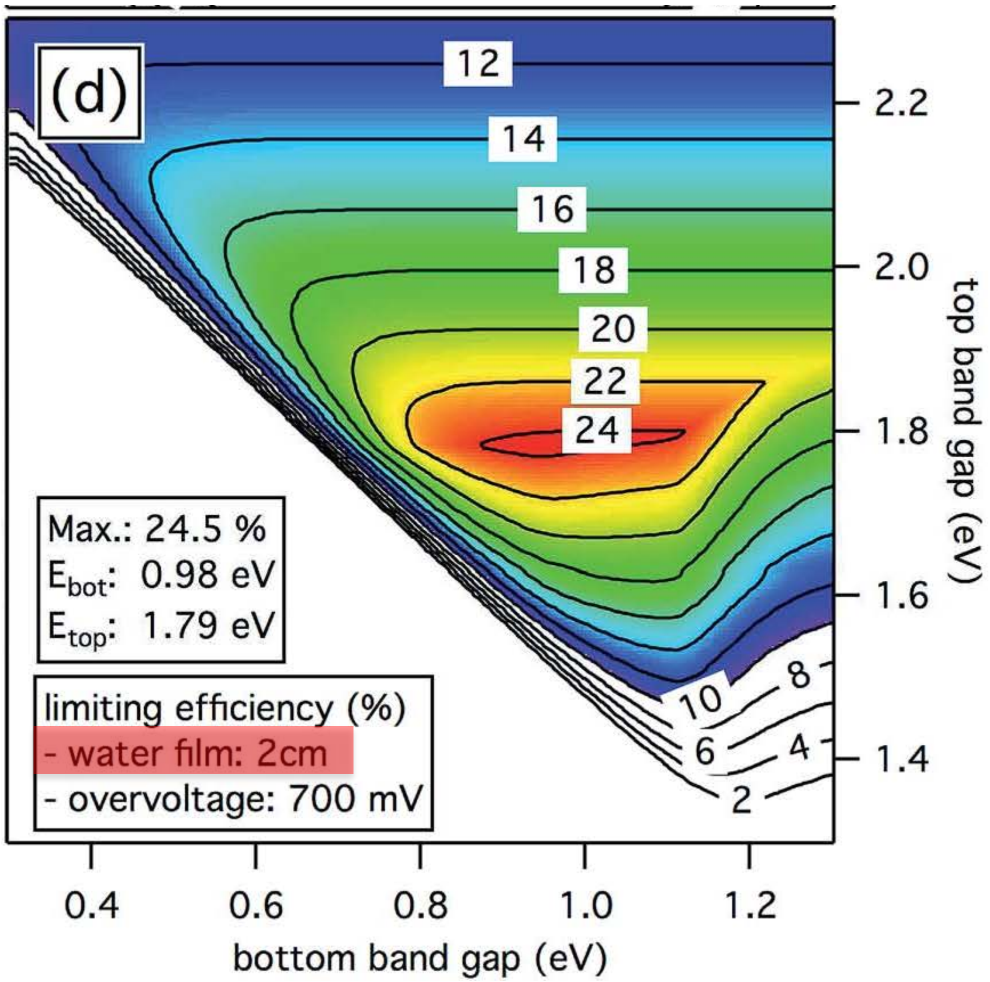
- **Tandem absorbers**
  - Task 1: Demonstrating attainable efficiencies
    - III-Vs by MOCVD (NREL)
  - Task 2: higher-risk, lower-cost approaches
    - $In_xGa_{1-x}N$ tandems (LANL)
    - III-V-N on Si tandems (NREL)
    - Coupled photoanode-photocathode systems (Hawaii, NREL)



- **Surface modifications – spectroscopy (UNLV) and modeling (LLNL)**
  - Ion-implantation & flash sputtering (NREL)
  - Thin coatings by atomic layer deposition (ALD) (NREL, CU)
  - Molybdenum disulfide (MoS_2) coatings (Stanford)
- **Benchmarking, prototyping, & demonstration**
  - Photoreactor design and outdoor device testing (NREL, JCAP-Solar Fuel Hub)

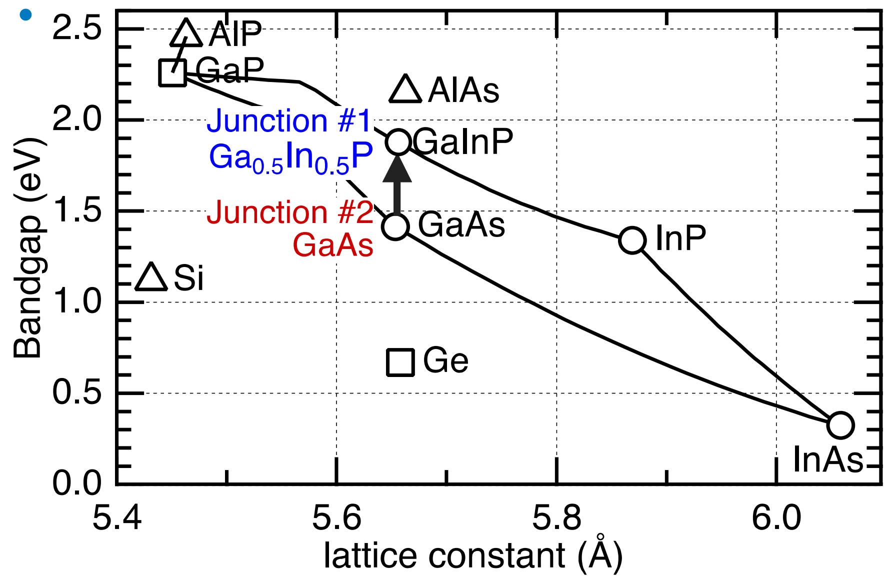
Approach: High Efficiency via Tandems

Döscher et al. *Energy Environ. Sci.*, **7** 2956 (2014)



- Exceeding 20% solar-to-hydrogen (STH) feasible
- Reactors with low water penetration for 25% STH
- $GaInP_2$/GaAs (1.8 eV, 1.4 eV) not optimal, 1.4 eV bottom band gap too high – limits current

- Traditional MOCVD requires lattice matching from substrate through all epi-layers to maintain high material quality
- Metamorphic growth removes "vertical-only" constraint by incorporating a transparent, step-graded layer to allow non-lattice matched absorbers
- Inverted Metamorphic Multijunction (IMM) growth: top junction grown first, device layers removed from substrate, could potentially be re-used
-



Approach: Surface Validation Team

Understanding and remedying semiconductor photocorrosion at PEC interfaces is a complex task that has benefitted significantly from a collaborative approach teaming experts with unique capabilities and resources

- **Heske group at UNLV**
  - XPS, XAS, XES, IPES, UPS, AFM
    - Some measurements at Advanced Light Source (ALS), Berkeley Lab
  - Snapshots of surface pre-, intermediate, post-exposure
  - Identify common features of and conditions that lead to corrosion
  - **<u>Characterize stabilized surfaces</u>**
    - Show where we are in parameter space wrt. amounts of N & PtRu

- **Ogitsu group at LLNL**
  - Develop theoretical tool chest for modeling PEC systems
  - Simulate x-ray spectra to correlate UNLV experimental results with surface/near surface compositions
  - Model III-V surfaces to uncover the key mechanisms of surface corrosion

PEC NREL

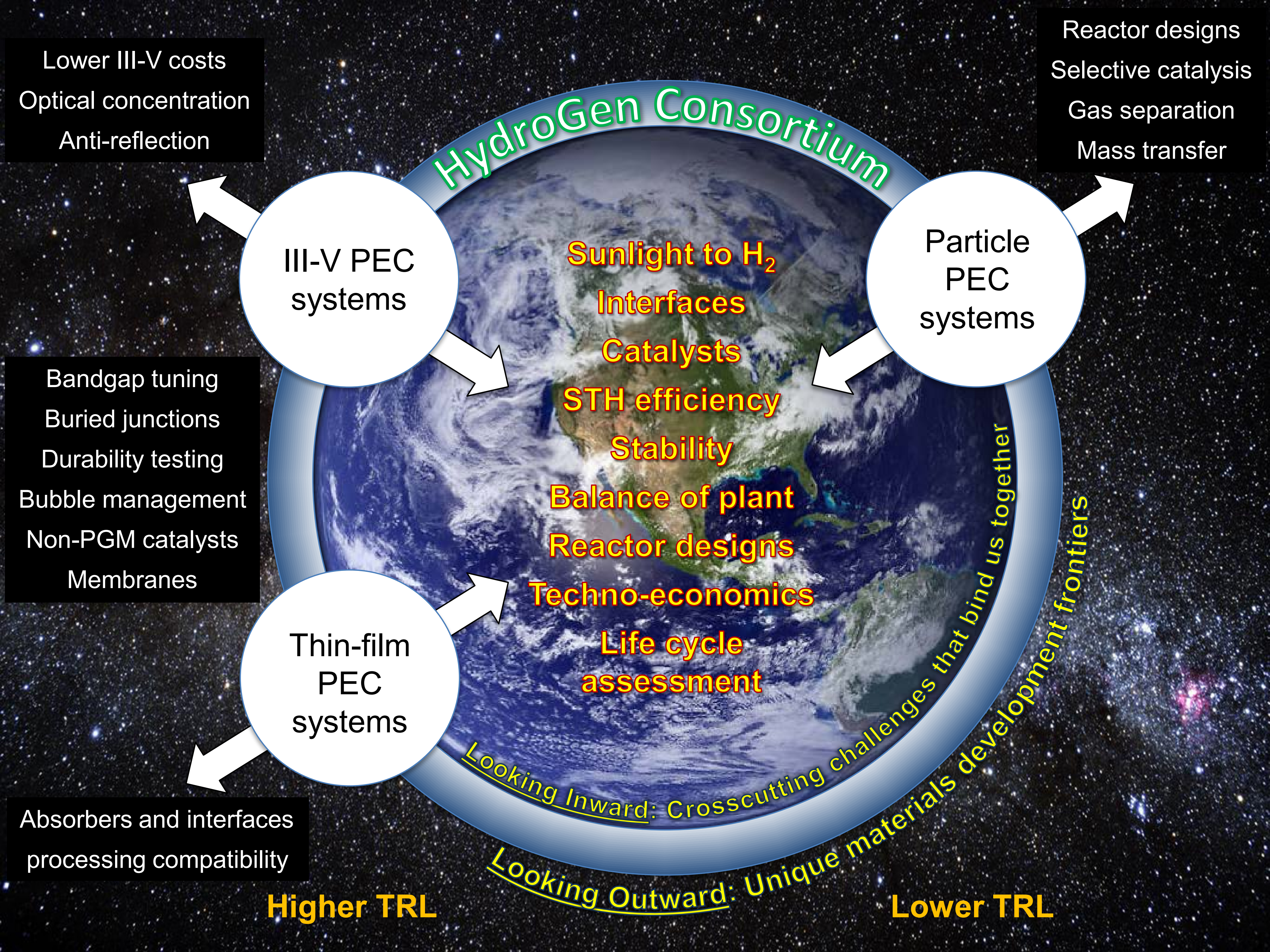
Spectroscopy UNLV

Theory LLNL

Approach: Milestones

Qtr	Due	Type	Milestones, Deliverables, or Go/No-Go Decision	Status
FY15Q3	6/30/2015	Regular	Show progress towards photoreactor prototype by demonstrating a feasible design that achieves 10x concentration	Complete
FY15Q4	9/30/2015	Annual/ Go / No-Go	Demonstrate greater than 15% STH at short circuit on an advanced III-V tandem structure. Verify that the average current density (in mA/cm^2) multiplied by the lower heating value of hydrogen (1.23 V) sustained over one hour in a zero-bias, two-terminal.	Complete
FY16Q1	12/31/2015	Regular	Perform technoeconomic analysis (TEA) on higher concentration systems (100x) and use H2A to generate a tornado plot that shows the sensitivity of a type 4 reactor to optical concentration. Complete a reactor design/engineering study that evaluates potential drop due to electrolyte Ohmic losses and feasible reactor geometries to identify the practical upper limit of concentrated PEC systems to input in to TEA.	Complete
FY16Q2	3/31/2016	Regular	Identify a wide-bandgap (1.5-1.8eV) semiconductor (n- or p-type) with suitable IPCE and below-bandgap transmission to serve as the top electrode for a dual photoelectrode system.	Complete
FY16Q3	6/30/2016	Regular	Validate Faradaic efficiency by measuring the H_2/O_2 ratio in PEC product gas stream mixed with inert sweeping gas using a capillary mass-spectrometer	On track
FY16Q4	9/30/2016	Annual/ Go/ No-Go	Using two-terminal J-V, validate over 15% STH on a surface modified electrode prior to durability testing. Durability testing will be performed potentiostatically or galvanostatically where the photocurrent should be maintained above 12 mA/cm^2 for 875 continuous hours under 1-sun illumination. Upon completion of durability testing, use two-terminal J-V to demonstrate that the surface modified electrode has experienced less than 20% loss in STH efficiency.	On track

All program milestones are completed or on-track for on-time completion.


HydroGen Consortium
Lower III-V costs
Optical concentration
Anti-reflection
III-V PEC systems
Reactor designs
Selective catalysis
Gas separation
Mass transfer
Particle PEC systems
Bandgap tuning
Buried junctions
Durability testing
Bubble management
Non-PGM catalysts
Membranes
Sunlight to H_2
Interfaces
Catalysts
STH efficiency
Stability
Balance of plant
Reactor designs
Techno-economics
Life cycle assessment
Thin-film PEC systems
Absorbers and interfaces
processing compatibility
Looking Inward: Crosscutting challenges that bind us together
Looking Outward: Unique materials development frontiers
Higher TRL
Lower TRL

Approach: Pathways to III-V Semiconductor Cost Reductions

- **Optical concentration**
  - 10x-500x uses less absorber
- **Reuse substrate**

  Woodhouse et al. Report NREL/PR-6A20-60126
  - Epitaxial lift-off

    Shermer et al., *PSSa* **202,** 501–508 (2005)
  - Multilayer epitaxial assemblies

    Kang et al., *APL* **102,** 253902 (2013)
  - Spalling

    Shahrjerdi et al., *APL* **100,** 053901 (2012)
  - Laser lift-off

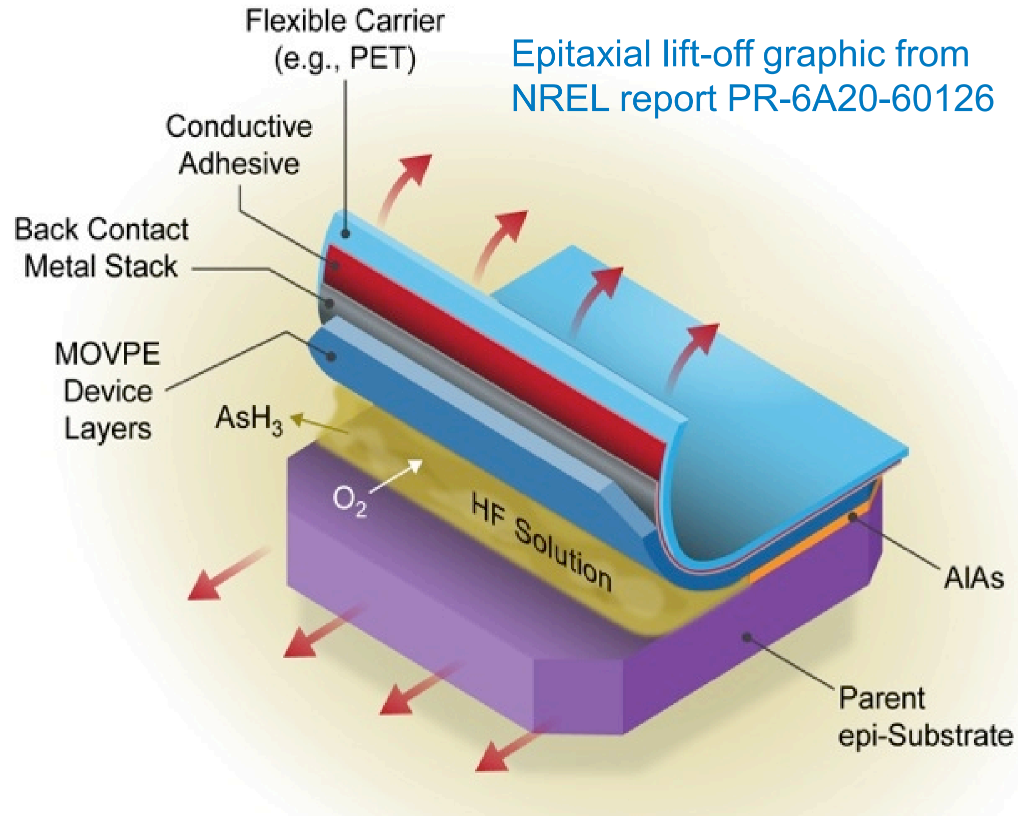
    Hayes & Clemens, *MRS Comm.* **5**, 1–5 (2015).
- **Alternative substrate**

  Woodhouse et al. Report NREL/PR-6A20-60126
  - III-V on Si

    Geisz & Friedman, *Semi. Sci. Tech.* **17,** 769–777 (2002)
  - Metal foil
    - Close-space vapor transport

      Kiriya et al., *JAP* **112,** 123102 (2012)
    - Ion beam assisted deposition

      Dutta et al., *APL* **105,** 092104 (2014)



Epitaxial lift-off graphic from NREL report PR-6A20-60126

- **Alternative precursors**
  - Close-spaced vapor transport

    Ritenour et al., *ACS AMI* **4,** 69–73 (2012)
  - Hydride vapor phase epitaxy

    Schulte et al., *JAP* **113,** 174903 (2013)

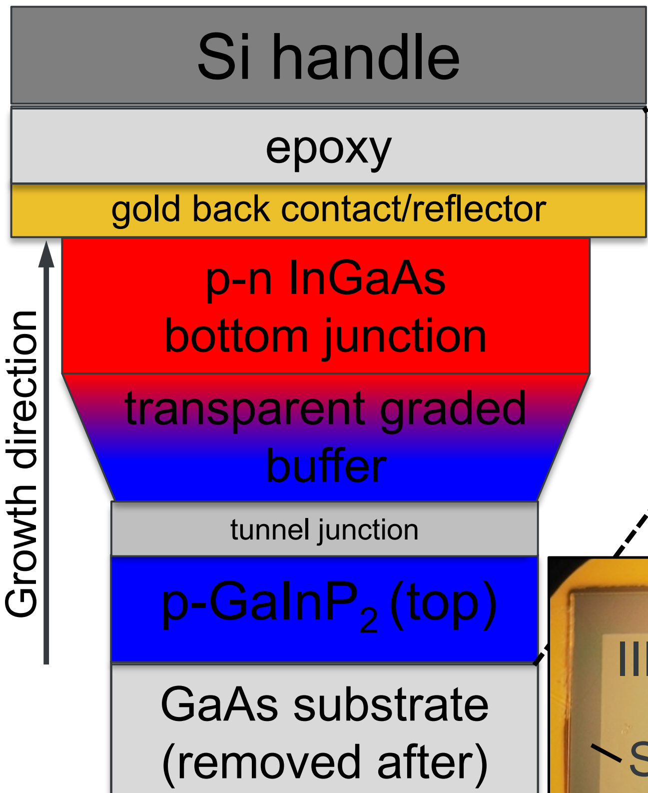
This is a very active area of research that includes commercial cell manufacturers and funding support from ARPA-E.

Inverted Metamorphic Multijunction (IMM) Cells for Unrivaled STH Efficiency

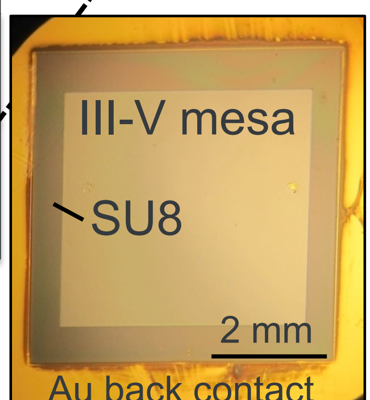
IMM grown by organometallic vapor phase epitaxy (OMVPE)

Metamorphic: graded lattice constant interconnect, minimizing defects

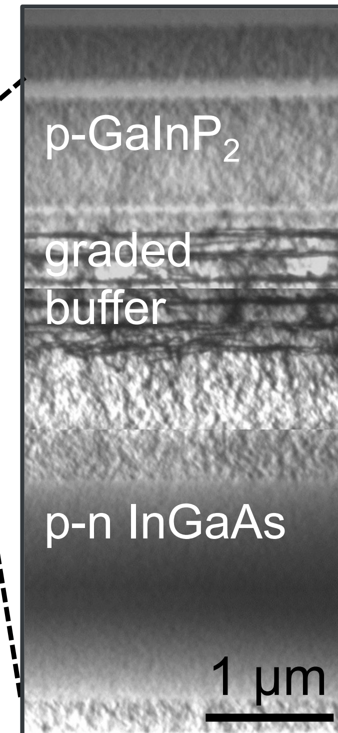
Inverted: top cell grown first, avoid lattice mismatch, can add back reflector



invert,
remove
substrate



SEM (*x-section*)



TEM

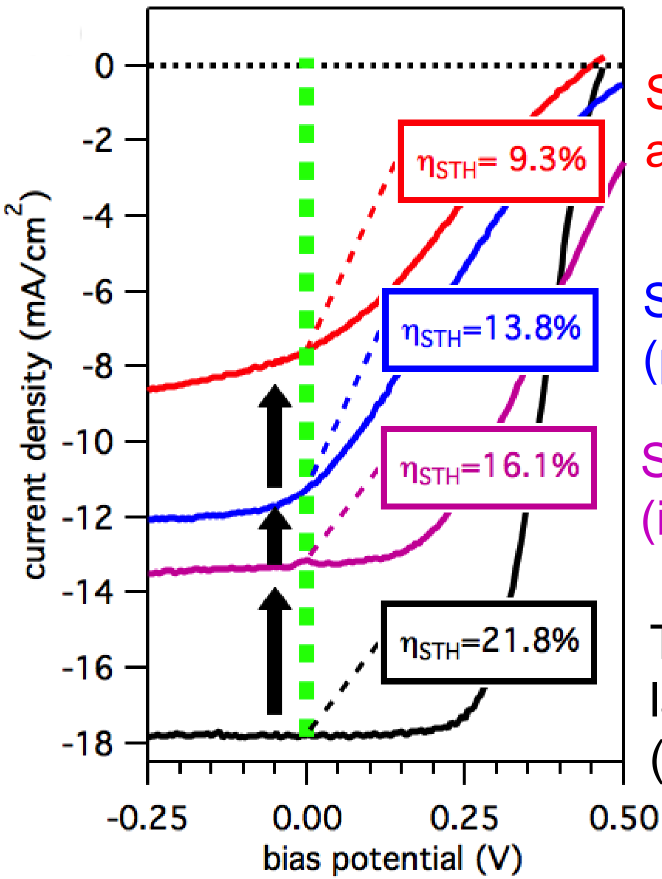
Growth: M. Steiner, R. France, W. Olavarria, M. Young

James Young

Andrew Norman

Progress: Benchmarking – Shining (Sun)light on STH Efficiency

Used classical $GaInP_2/GaAs$ tandem to demonstrate potential sources of error

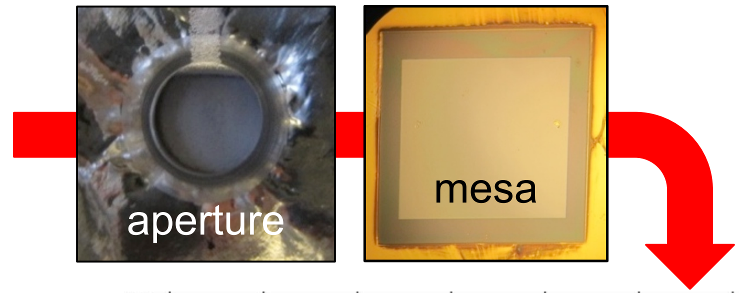


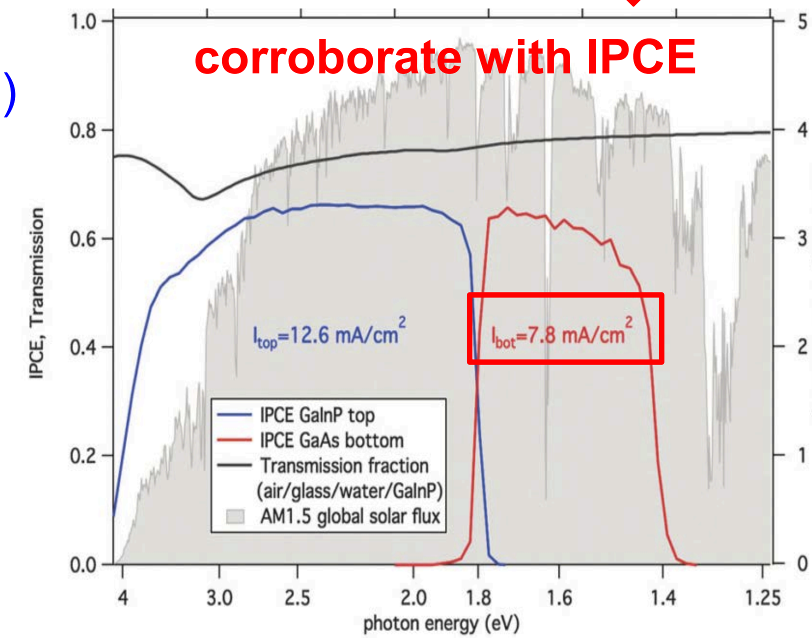
Sunlight: direct, area well-defined

Sunlight: direct (poorly-defined area)

Sunlight: global (indirect light paths)

Tungsten-halogen laboratory source (spectral error)



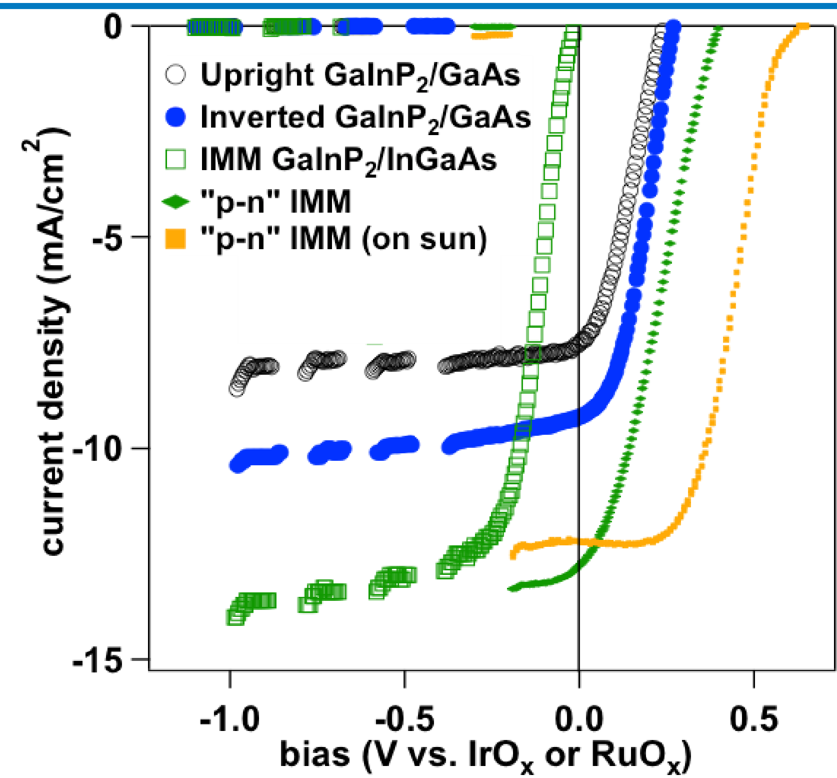


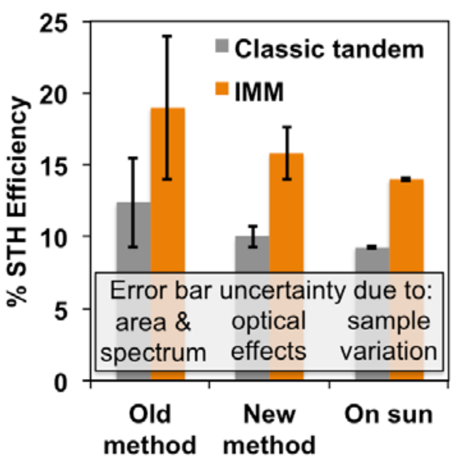
H. Döscher†, J. L. Young†, J. F. Geisz, J. A. Turner, and T. G. Deutsch, "**Solar to hydrogen efficiency: Shining light on phoelectrochemical device performance**," *Energy and Environ. Sci*. **9**, 74-80 (2016).

Progress: World Record STH Efficiency with Buried Junction IMM Cell

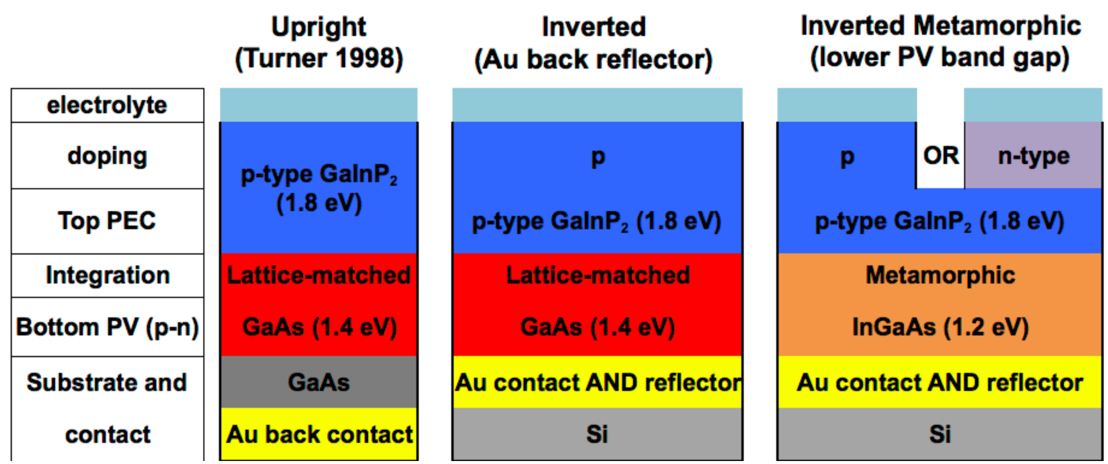
Improvement in STH efficiency

- Augmented voltage of IMM cells by incorporating a p/n buried junction
  - Light-limited current achieved at short circuit
- Measured 16% using solar simulator
- Achieved 14.3% STH under outdoor, direct solar measurements
  (NEW WORLD RECORD!!!)
- Notable unbiased STH achievements
  - 12.4 % STH: 1998, upright $GaInP_2/GaAs$
    Khaselev & Turner, *Science*, **280**, 425 (1998)
  - 14 % STH: 2015, upright metamorphic $GaInP_2/InGaAs$
    May et al., *Nature Communications* **6**, 8286 (2015)
  - 14.3 % STH: 2016, IMM (this work)



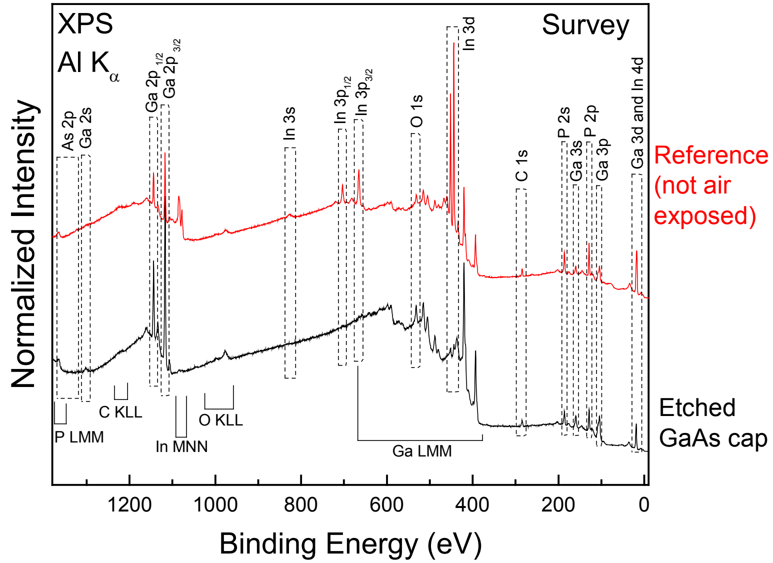


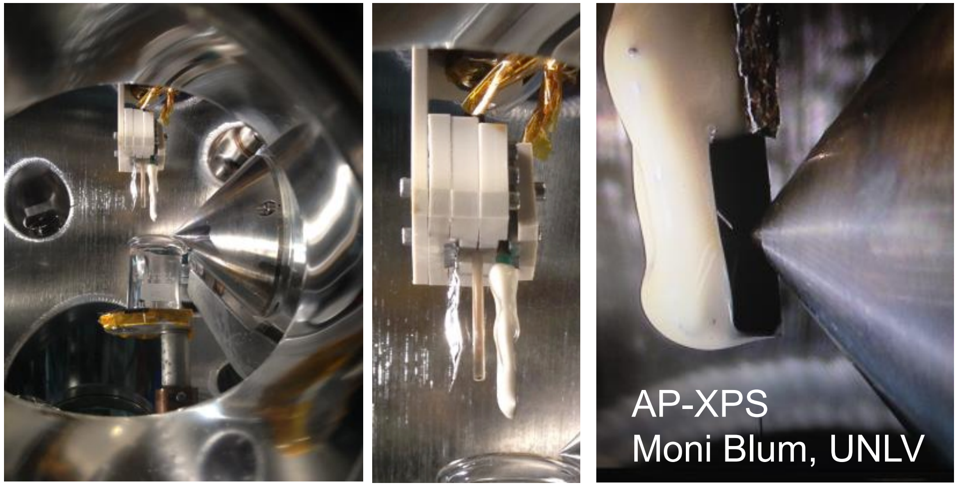
Qualitative view of STH error bars with continued refinement of measurements:
Old = epoxy & tungsten light
New = mesa isolated & combined W/Xe simulator
On sun = mesa isolation & direct beam sunlight



Progress: Identifying Key Characteristics of Relevant New Semiconductor Surfaces

Surface Validation Team quickly pivots to new material and supplies meaningful results





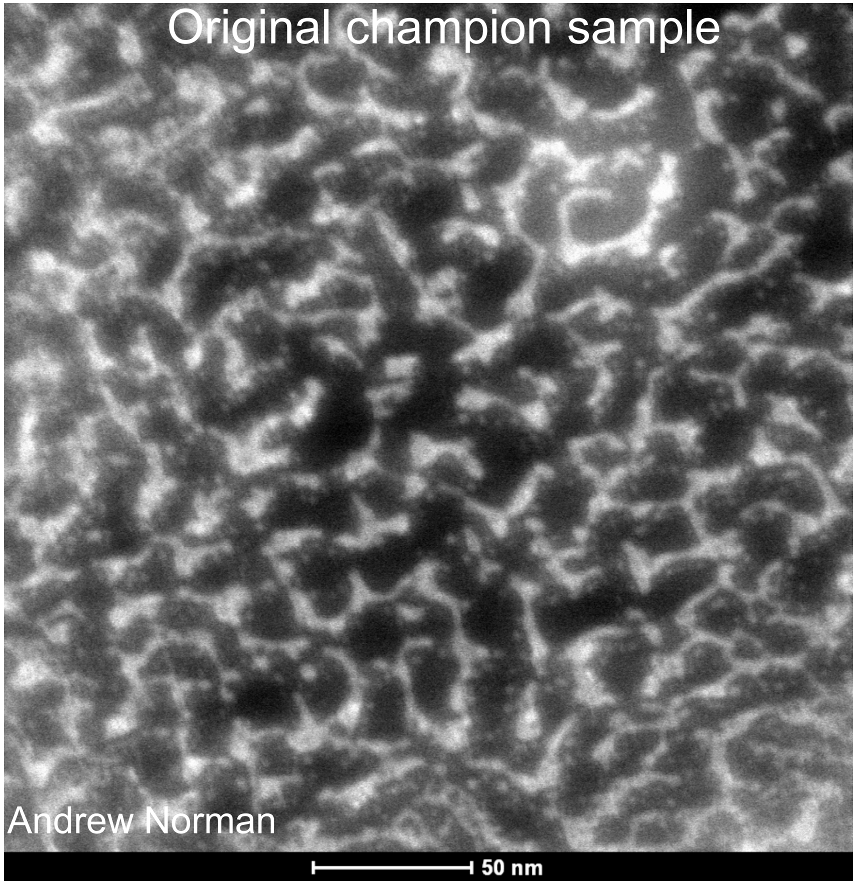
- Stability dictated by semiconductor surface
- IMM surface is very different from previous upright surfaces
  - Previously p-$GaInP_2$ that was an epitaxial surface, exposed to MOCVD chamber ambient during cool-down
  - IMM surface is n-$GaInP_2$ for buried junction cells and was encapsulated by other layers during cool-down, revealed by post growth *selective* etching of the GaAs substrate
- IMM cells sent to UNLV for spectroscopic characterization of surfaces after removing substrate capping layer – expected clean $GaInP_2$ surface
- XPS by UNLV: Ga, P surface, along with C, O, **but no In**
- Compared to reference p-$GaInP_2$ surface grown/extracted/stored without air exposure

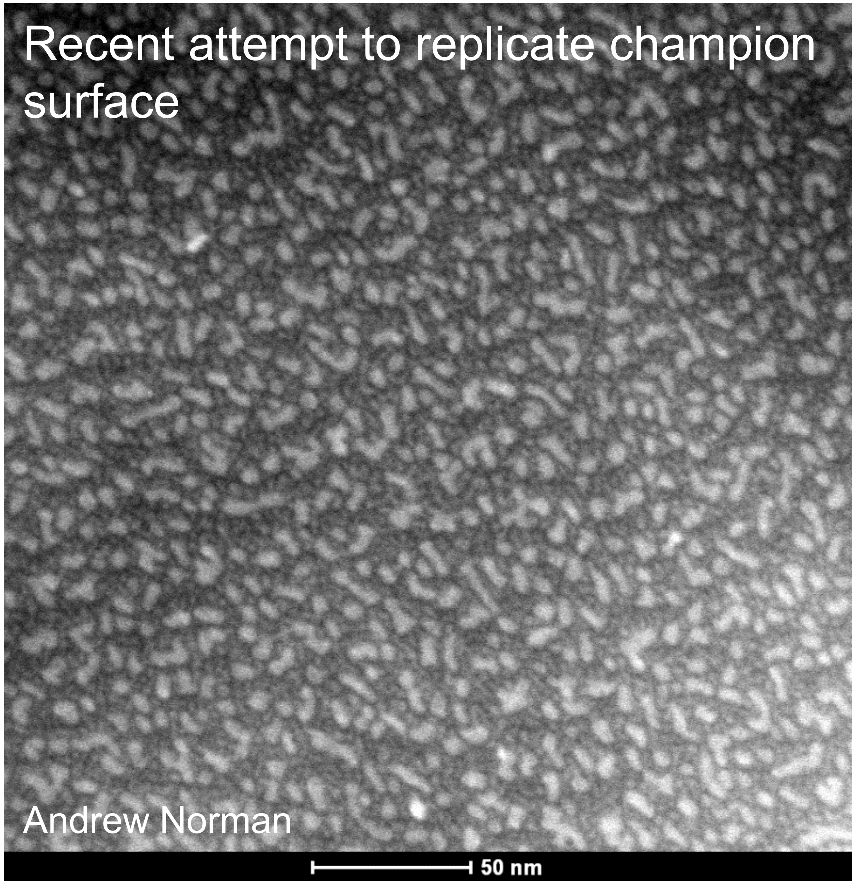
Near future plans (UNLV & LLNL)

- Ambient Pressure X-ray Photoelectron Spectroscopy (AP-XPS) at ALS
  - ***Operando*** observation of dynamic surfaces
- Measure electronic structure of n/p-$GaInP_2$ buried junction (VBM, CBM, work function)
- GW Approximation (beyond DFT) calcs to enhance confidence in interpretation of spectroscopic operando measurements
  - Excellent agreement demonstrated on surface orientation dependence of band edge positions in electrolyte (InP(110)) [Stevanovic et al. PCCP **16**, 3706 (2014)]
  - Effect of electrolytes on InP(001) band edges [Pham, Wood, Ogitsu, in preparation]

Progress: Identified Surface Characteristics of Champion Durability Electrodes

Observed microstructure of champion electrode surface to guide attempts to replicate



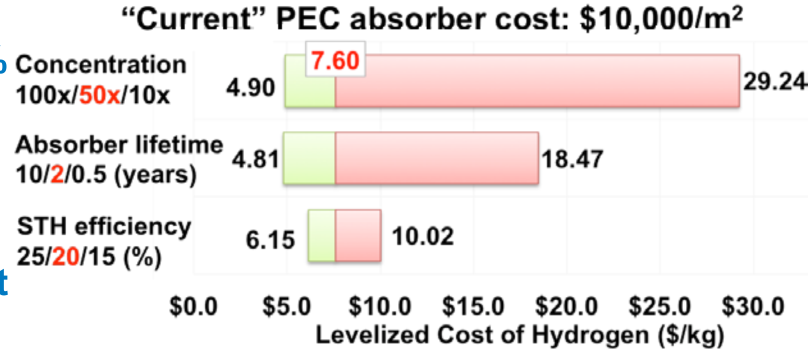


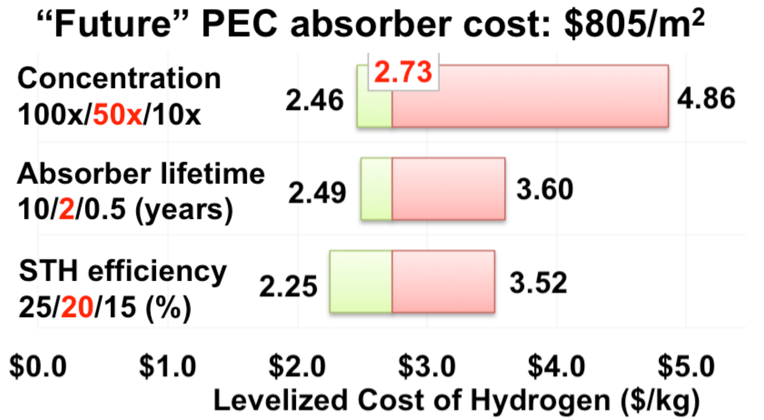
- "champion" N_2^+ ion bombarded and PtRu sample had exceptional stability yield (all electrodes stable) – only some electrodes from more recent samples where we attempted to replicate the surface exhibit stability
- UNLV XPS and XES results indicate champion sample has 10x less PtRu and 10x more nitrogen content
- Sacrificed the last untested champion sample for destructive microscopy to understand parameter space
- Scanning Transmission Electron Microscopy High Angle Annular Dark Field (STEM HAADF) shows small bright features suggesting particles of higher atomic number as would be expected for Pt/Ru

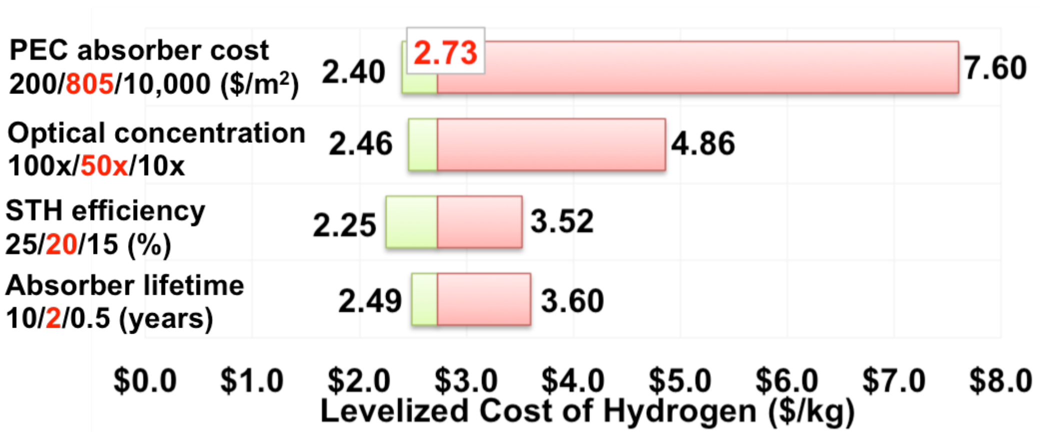
Progress: H2A Modeling of Concentrator Cells

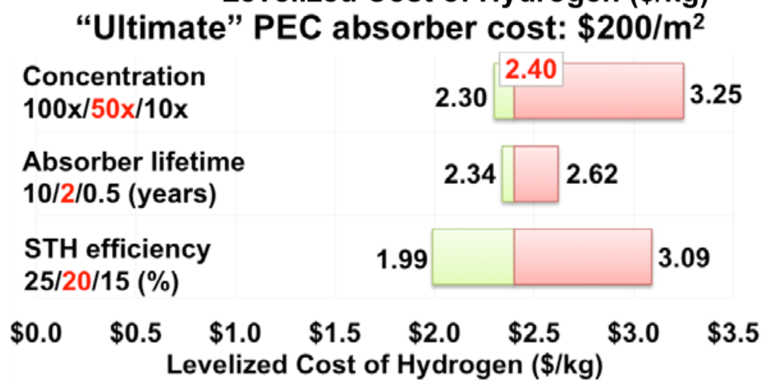
H2A modeling shows optical concentration can mitigate effect of high absorber costs in near term

- **H2A version 3.0 Type 4 PEC case study**
- **1 TPD plant, scaled to 2 TPD, 98% operating capacity, 25% solar capacity factor**
- **Capture areas for 1 TPD**
  - 15% STH: 27,199 m^2 (5 football fields); 20% STH: 20,400 m^2 (4 football fields);25% STH: 16,320 m^2 (3 football fields)
    - 2.13 x 10^{-6} $kg.m^{-2}.s^{-1}$ rate for 25% STH
- **Lenses (Fresnel w/ secondary) = \$75/m^2, 10-y replacement**
  - Multiplied by entire capture area; considered 10x, 50x (base case), 100x
  - Absorber area = Capture area/concentration
- **Plexiglas = \$124/m^2, 10-year replacement**
  - Multiplied by 3*(absorber area)
- **To date, most H2A models have very optimistic assumptions of absorber costs – most critical parameter**
- **Performed sensitivity analysis using more realistic costs: "current", "future", "ultimate"**
  - Near term: concentration is largest lever – absorber costs dominate
  - Long term: Efficiency is the greatest lever – BOS costs dominate







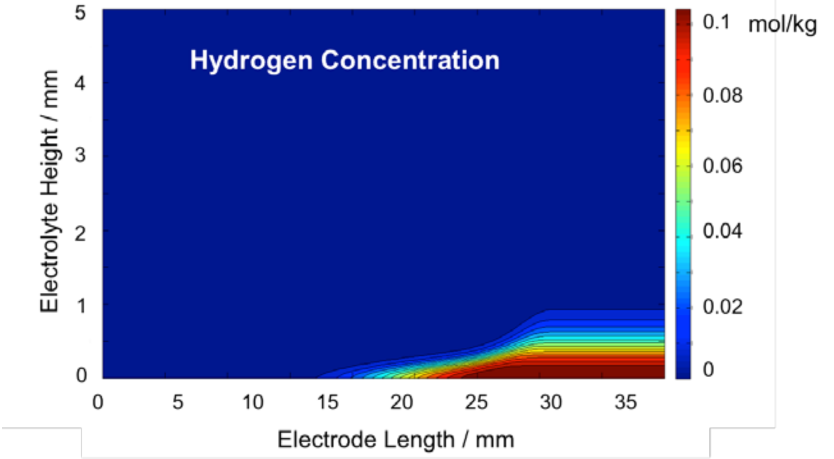


Progress: Multi-physics Modeling of 10x Concentrator Cells and Prototype Fabrication for On-Sun Measurements

Modeling of PEC reactor shows 10x concentration is feasible; prototype made, tracker purchased

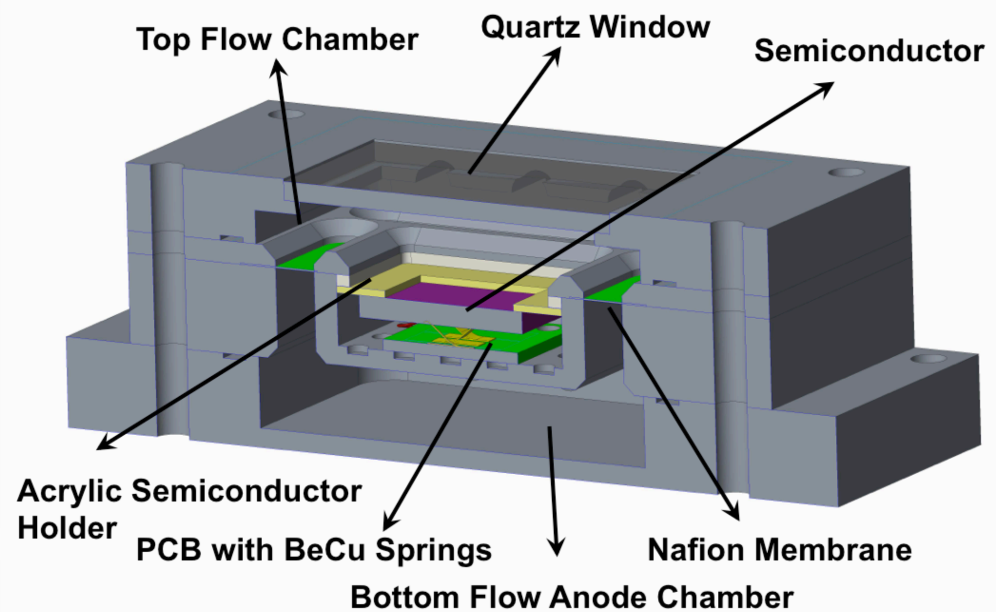
COMSOL on NREL's supercomputer

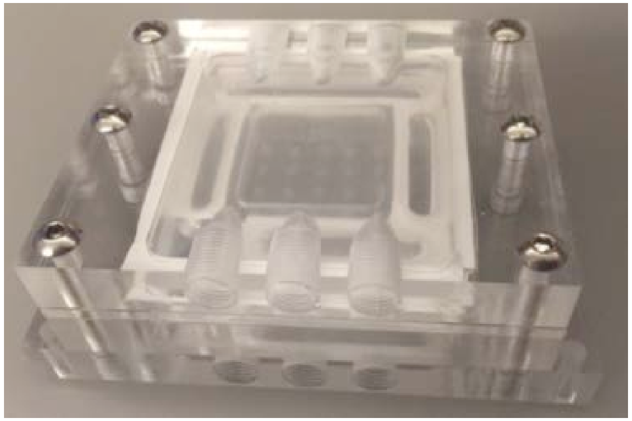
- Laminar flow in PEC chamber
- H_2 concentration
- Optical path through electrolyte
  - ≤5 mm electrolyte thickness
- H^+ / HSO_4^- distribution
  - Potential drop through electrolyte ~300 mV
- Overvoltage
  - ~80 mV (HER) + ~220 mV (OER) + 300 mV (solution)
  - Total voltage necessary = ~1.85 V



Only first 30 mm include generation: flow left→right 30 mm/s (avg)
Minimum pressure to keep hydrogen in solution : **147 atm**

Using pressure to keep H_2 from bubbling and scattering light is not feasible under these conditions





Prototype chassis machined from PMMA
Concentration via Fresnel lens mounted to reactor

Progress: Responses to Previous Year Reviewers' Comments

- "On the topic of light concentration, it is not clear how sensitive the H2A analysis is to light concentration…this reviewer has not seen an H2A analysis (i.e., Tornado plot) showing how sensitive the Type 4 hydrogen cost is to light concentration. This would be valuable to know."
  - Response: We have included several tornado plots for a type 4 (concentrator) PEC reactor that shows the sensitivity of hydrogen cost projections to various optical concentration factors on slide 17.

- "Having a significant solar concentration level is a central ingredient of this project. In this regard, thermal management is likely to be a limiting feature for photoreactor design options. The project might be improved significantly by including design and engineering work to evaluate thermal management issues."
  - Response: The reviewer raises a valid concern. JCAP North recently published a computational study on hourly temperature profiles in a 10x concentration photoreactor (Stevens and Weber, *J. Electrochem. Soc.*, **163** (7) H475-H484 (2016)). Temperatures exceeded 100°C for 12 hours over a year of simulated operations only under extreme (no wind) conditions. With higher concentration levels, we will have to consider designs that use flowing electrolyte as active cooling and/or design photoreactors where sunlight does not pass through electrolyte.

Collaborations

- Partners (extensive collaboration with all)
  - University of Nevada Las Vegas
    - Partner in surface validation project
  - Lawrence Livermore National Laboratory
    - Partner in surface validation project
  - University of Hawaii (PD116)
    - Gaillard group – Partner on dual photoelectrode approach; sample exchange and validation
  - Los Alamos National Laboratory
    - Mark Hoffbauer – InGaN samples
  - Stanford University (PD119)
    - Jaramillo group – Key partner in MoS_2 for stabilization efforts
    - Joint publication MoS_2 on $GaInP_2$
  - Philipps-Universität Marburg, (Germany)
    - Henning Döscher, Marie Curie fellow, is a member of our PEC group and NREL's III-V group
  - Technical University of Denmark
    - Ib Chorkendorf – sample exchange
  - Joint Center for Artificial Photosynthesis (North)
    - Ian Sharp, Karl Walczak – sample exchange, benchmarking cross-validation
  - University of Toledo (PD118)
    - Yanfa Yan – sample exchange, joint manuscript
  - Colorado School of Mines
    - Electron microscopy and XPS user facilities
  - University of Colorado-Boulder
    - Shared grad student with Prof. Steve George is now PD in our group
    - Colorado Nanofabrication Lab – undergraduate working on dry etching for black-III-Vs
  - University of Louisville
    - Sunkara group – novel III-Vs ($GaAs_xSb_{1-x}$, $GaSb_xP_{1-x}$)
    - Joint characterizations/publications

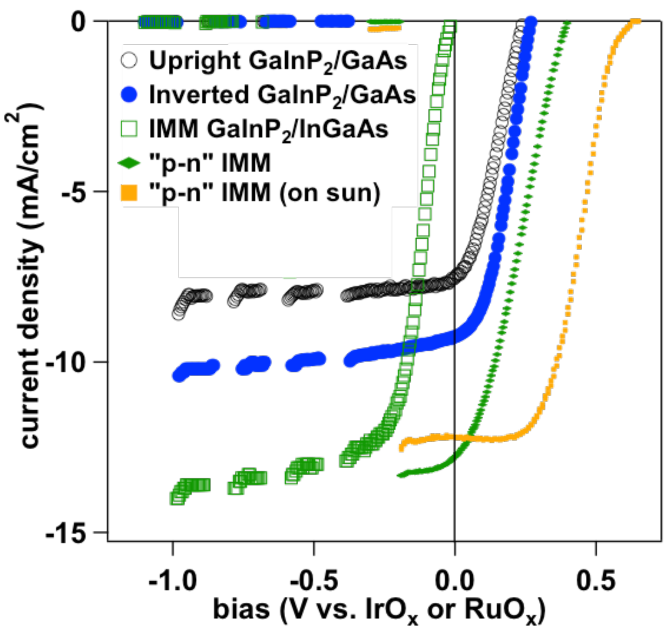
Remaining Challenges and Barriers

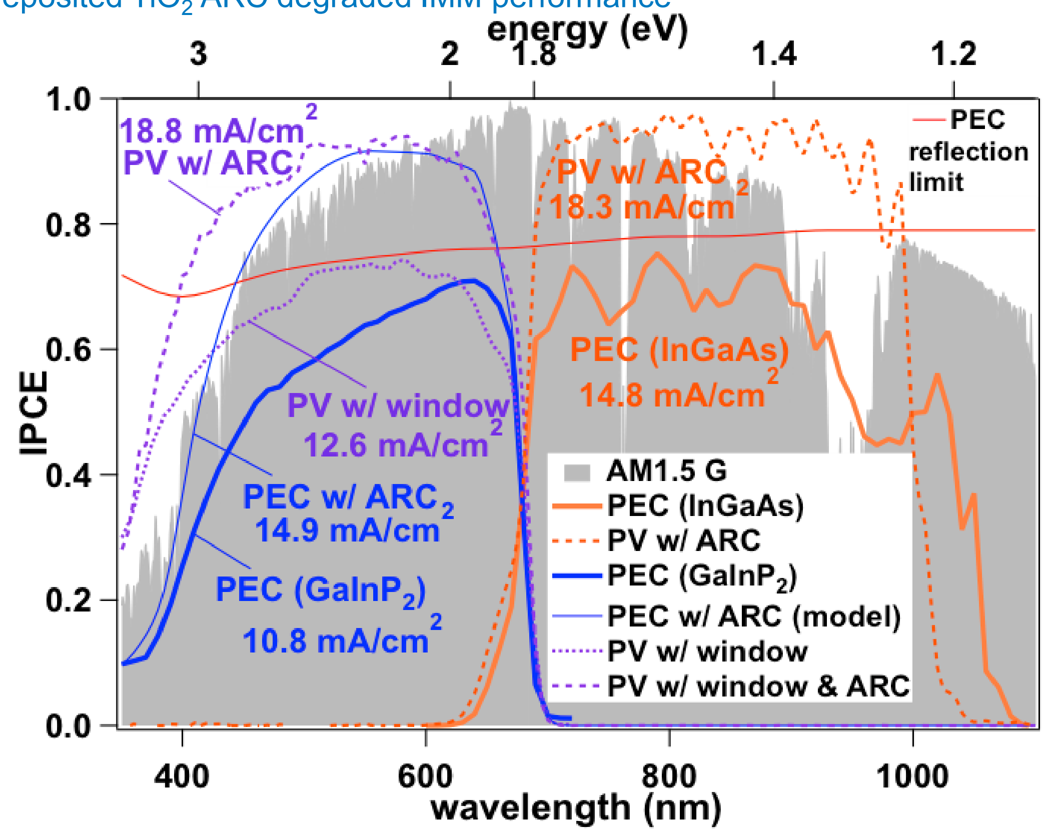
- **Efficiency:**
  - Push solar-to-hydrogen efficiency from ~~12%~~ (~10%) to beyond 20% for meeting ultimate DOE targets
- **Durability:**
  - More realistic real-world durability assessments – none of the reported impressive 100+ hours in biased three-electrode tests translate to true unbiased two-electrode configurations
  - Buried junction eliminates requirement of contact with electrolyte to generate electric field – relaxes constraints on protective coating
  - Investigate encapsulated IMMs to achieve over 850 hrs @ 15%
- **Semiconductor costs:**
  - Reduce synthesis costs by factor of 10 compared to current cost of small-batch III-V materials
- **System testing:**
  - Test promising photoreactor designs and components on solar tracker
    - Window/body material, sealant/epoxy, membrane, counter electrode

Future Work: Increase STH Efficiency

Plans to increase STH efficiency with III-V IMM cells

- Overall device current limited by top ($GaInP_2$) junction
- Buried (p-n) junction leads to loss of higher energy photons which reduces photocurrent density
  - Electric field at n-$GaInP_2$/electrolyte interface pushes charges in wrong direction,
- Solid-state AlInP "window layer" can passivate surface, increase harvest of UV photons and raise photocurrent by 1 mA/cm^2
- Biggest loss is reflection at semiconductor surface: Optimized anti-reflection coating (ARC) can increase photocurrent 2-3 mA/cm^2
  - Thin layer (TiO_2): First attempts at atomic layer deposited TiO_2 ARC degraded IMM performance
  - Nanostructured surface, similar to black Si
- Reduce top bandgap to 1.7eV





Future Work– Towards *Economical* Hydrogen

In order to achieve the EERE plant-gate, untaxed cost targets of \$1-2/kg H_2 (1kg H_2 = 1gge) requires a PEC system that uses 10x concentration, has 25% solar-to-hydrogen (STH) efficiency, a semiconductor cost around \$150/m^2, and 10 years of stability. With suitable concentration (>100x), cost target can also be met with higher absorber costs (\$805/m^2) and shorter (2 y) lifetime.

- **Efficiency**
  - Validate >15% STH efficiency on-sun at short circuit, 20% stretch goal
  - Push efficiency by incorporating PV techniques (window layer, contact layer, ARC) and testing lower bandgap configurations that sacrifice voltage to achieve higher currents (efficiencies)
- **Durability**
  - Continue evaluating surface protection approaches and investigate novel encapsulation concepts
  - Demonstrate over 875 hours of durability on 15% efficient encapsulated IMM at short circuit
- **Semiconductor Cost**
  - Test photoreactors with higher concentration to evaluate what levels are practically achievable under various configurations
  - Obtain samples for PEC characterization from innovative III-V synthesis routes being developed by other DOE programs (SunShot, ARPA-E)
    - Epitaxial lift-off, spalling, HVPE, CSVT
- **Photoreactor Prototyping**
  - Test photoreactors with optical concentration and low or no electrolyte penetration depth for on-sun measurements on a solar tracker.

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: Established and published efficiency measurement protocols for multijunction water splitting systems; improved voltage and current of IMM III-V devices and set a new **world record** at 14.3% STH; with UNLV, identified chemical nature of new material (n-$GaInP_2$) that interfaces with electrolyte; with UNLV and LLNL, initiated AP-XPS for operando corrosion investigations; observed catalyst distribution and microstructure of champion N_2^+/PtRu durability electrode; performed H2A sensitivity analysis for type 4 systems with moderate light concentration; modeled losses and H_2 concentration in a 10x photoreactor; discovered and published mechanism of intrinsic p-GaAs stability; with Stanford, submitted manuscript on MoS_2 stabilizing p-$GaInP_2$ surface for 60 hrs.

Collaborations: Several ongoing, active collaborations with synthesis, modeling, and characterization groups

Proposed Future Work: Push STH efficiency limits with IMM III-Vs; examine stacked mechanical (dual electrode) tandems with Hawaii; push three surface passivation approaches (N_2^+/PtRu, MoS_2, ALD TiO_2) and encapsulation pathways to achieve over 875 h durability; commence regular outdoor testing on solar tracker with higher concentration factors

Technology Transfer Activities

- **Currently responding to examination of non-provisional patent filed in 2014 on nitridation/sputtering surface protection**

Stable photoelectrode surfaces and methods

Publication number: US 20140332374 A1

ABSTRACT

Disclosed herein are methods of treating a semiconductor surface by nitridation and deposition of a ruthenium alloy. Also disclosed are semiconductors treated with these methods, their incorporation into photoelectrochemical cells, and their use in photoelectrochemical water splitting.

- **Non-provisional patent filed on using inverted metamorphic multi-junction III-Vs to achieve maximum attainable STH efficiency (March 2016)**

Acknowledgements

- James Young – NREL
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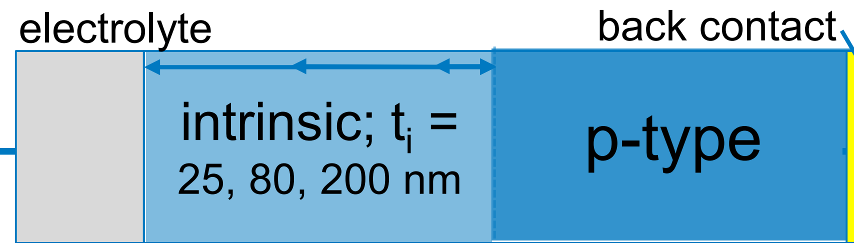
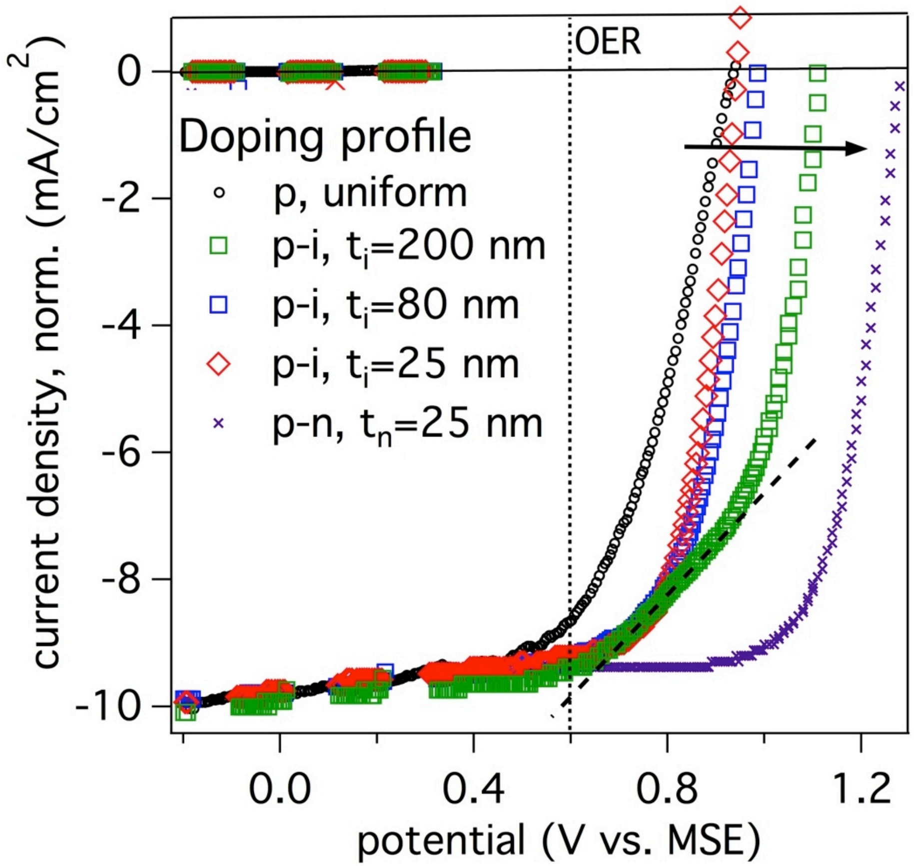
- Myles Steiner – NREL – IMM growth/modeling
- Anthony Abel – Drexel University (UG) – COMSOL modeling
- Ellis Klein – NREL – photoreactor fabrication/testing
- Huyen Dinh – NREL
- Arrelaine Dameron – NREL- PtRu sputtering chamber
- Andrew Norman – NREL- STEM
- All of our amazing collaborators noted throughout this presentation

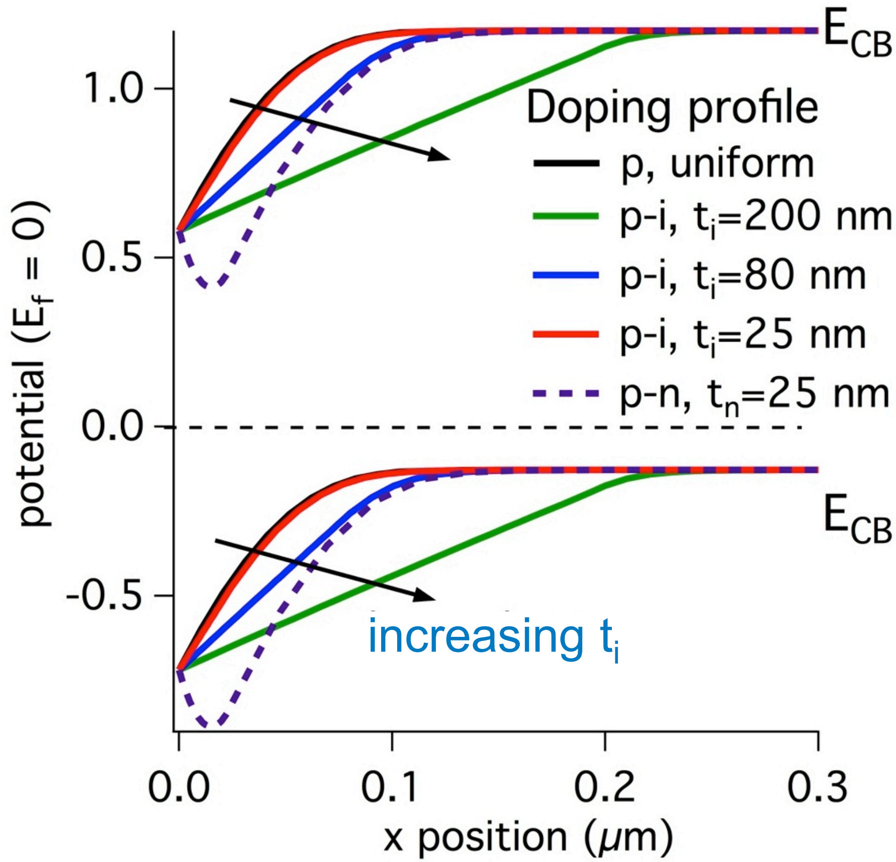
Technical Back-Up Slides

"p-i, p-n" Doping Profile



I-V characterization





Photovoltage increases with t_i, but Ohmic knee appears for high t_i

Depletion width increases with t_i

All "p-i" samples significantly exceeded by **"p-n" sample**

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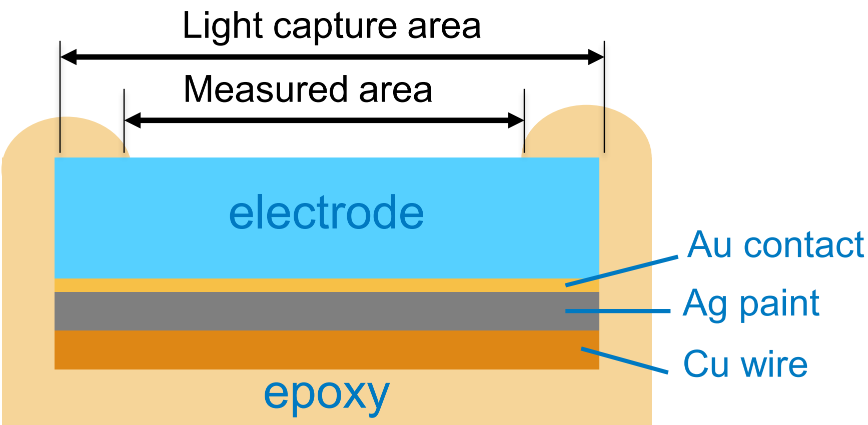
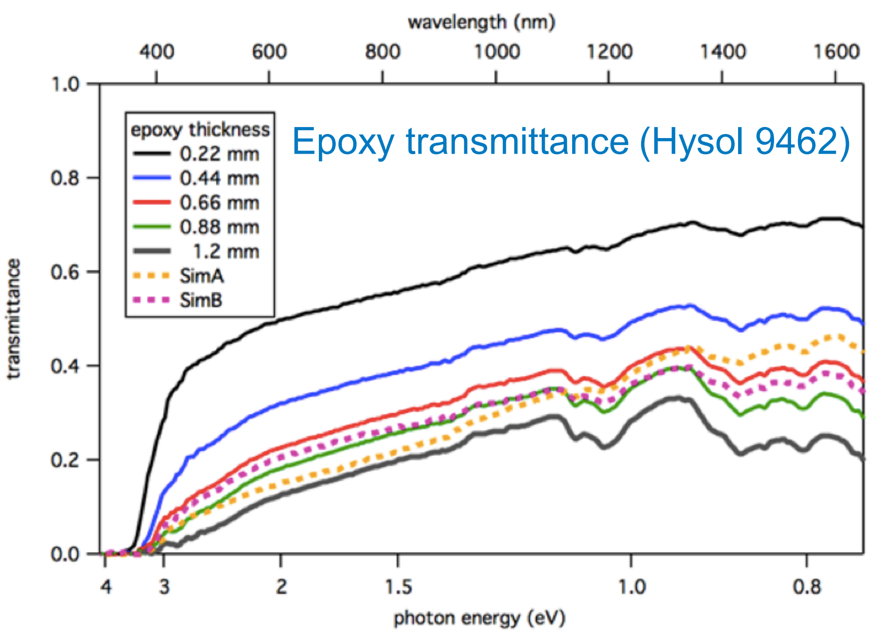
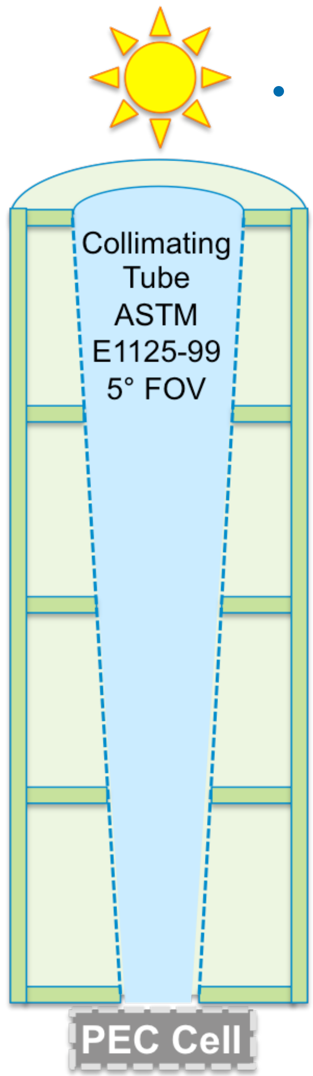
Minimizing Measurement Errors

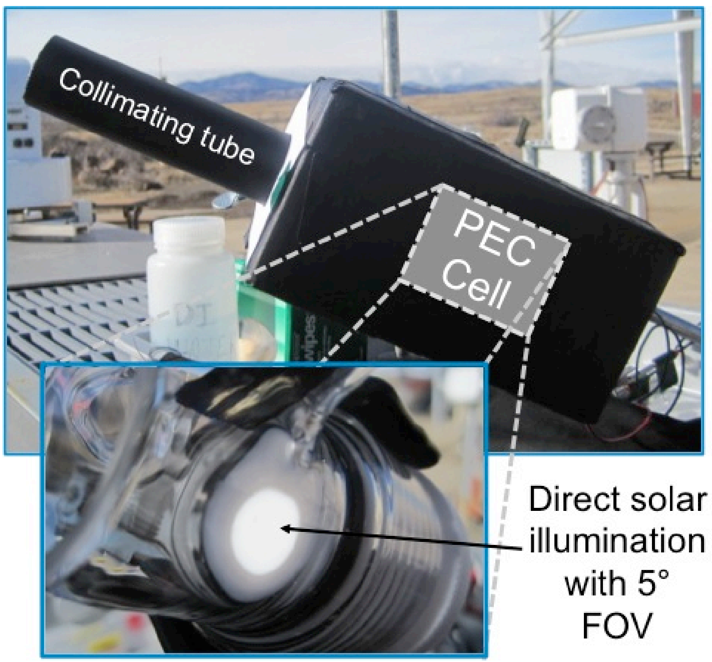


Electrode cross-section





- Epoxy commonly used to define “active” electrode areas is partially transparent
  - Underestimates light capture area
  - Leads to overestimated efficiencies
- Indirect (scattered) illumination can be coupled to the semiconductor by PEC cell components and overestimate efficiency
  - Solution: Collimating tube to exclude scattered light
  - Direct component of solar spectrum used for efficiency calculations



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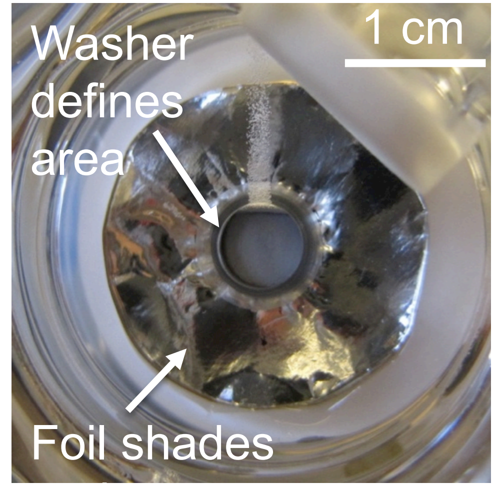
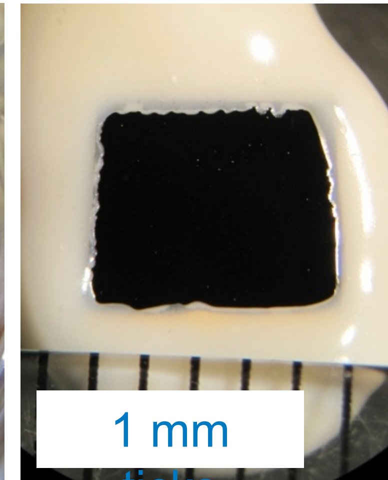
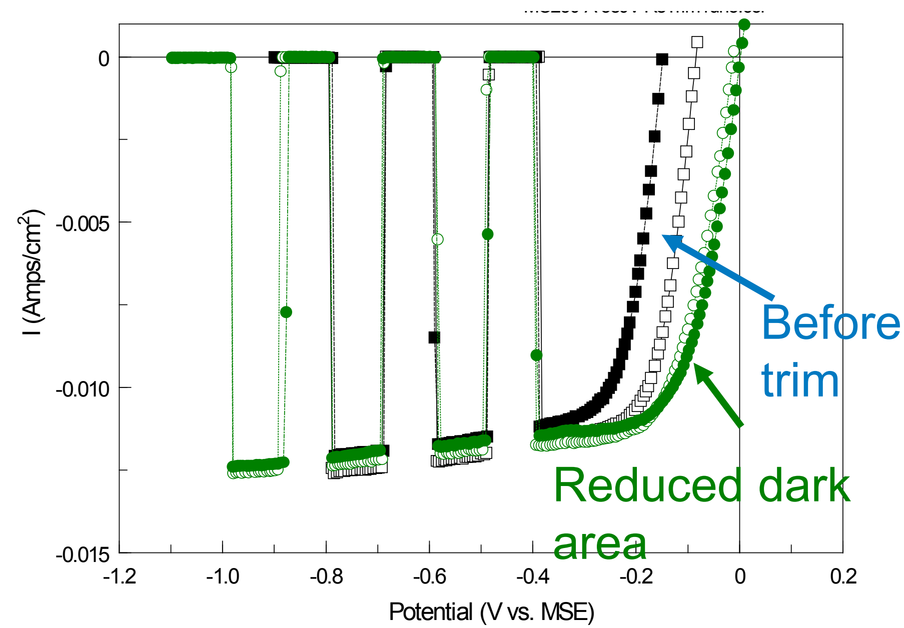
Addressing Measurement Error

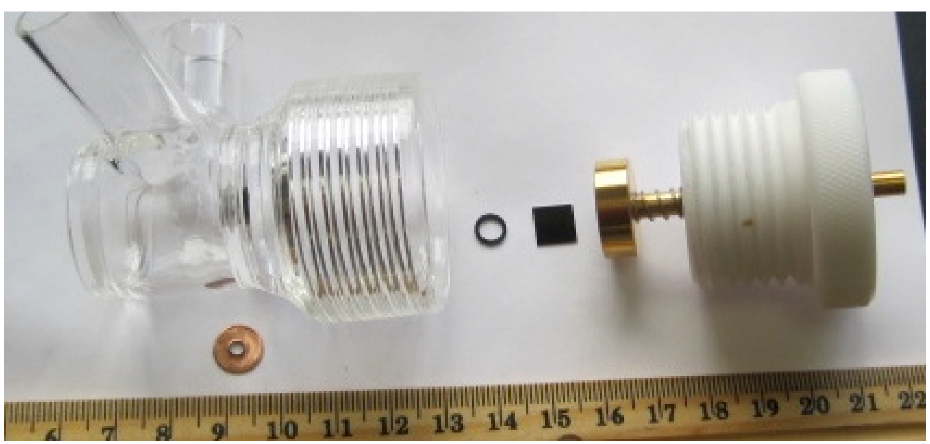
Area definition

- Compression cell
  - Area defined precisely by black washer and foil
  - BUT, large dark area compromises V_{oc}
    - $V_{OC} \sim \log (J_{light}/J_{dark}+1)$
  - ~ 2 cm optical path length through electrolyte attenuates IR photons necessary for current matching bottom junction
- Entire chip now used as device area, minimize epoxy coverage
  - Most conservative definition
  - Risks shorting by electrolyte









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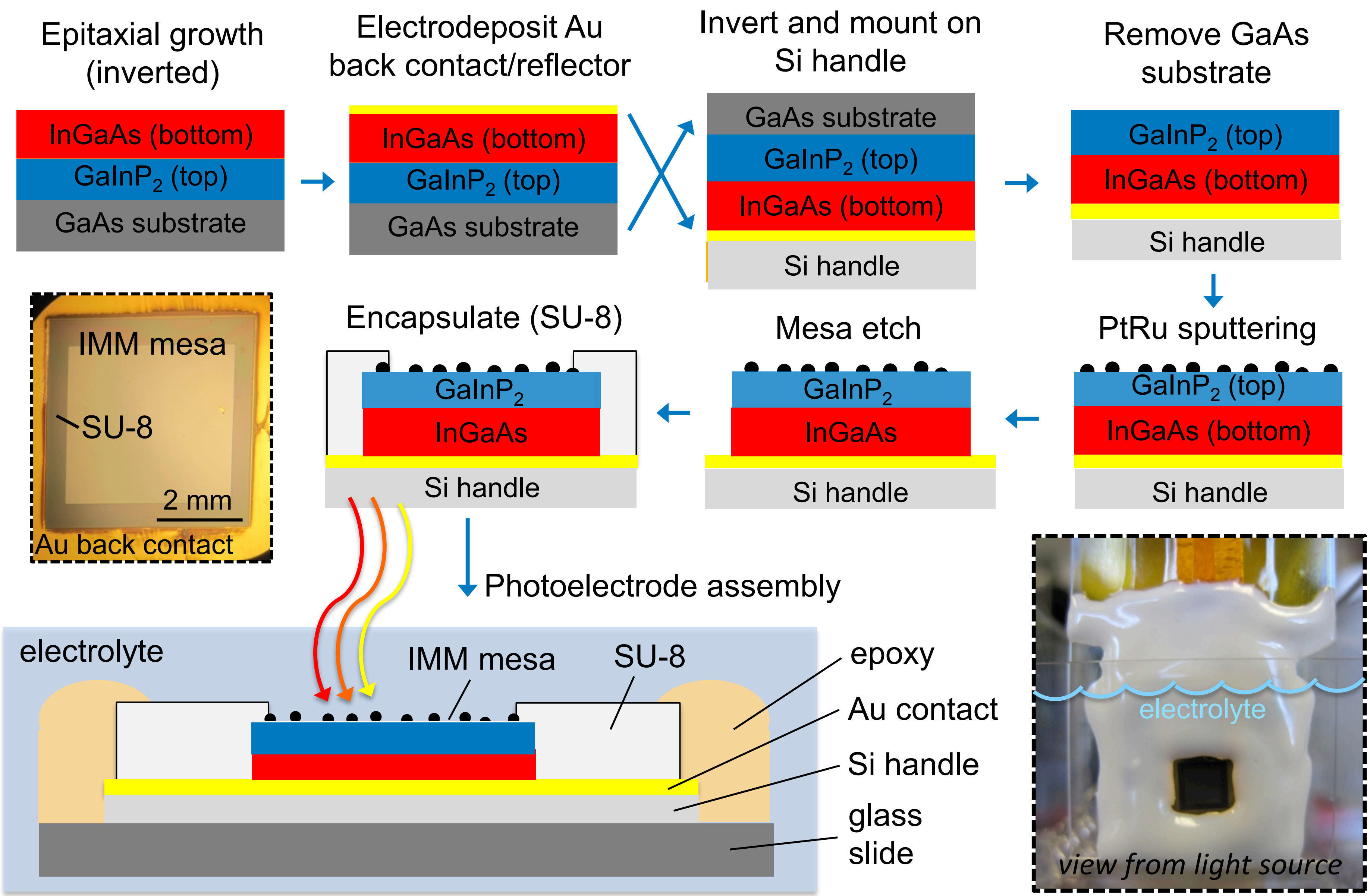
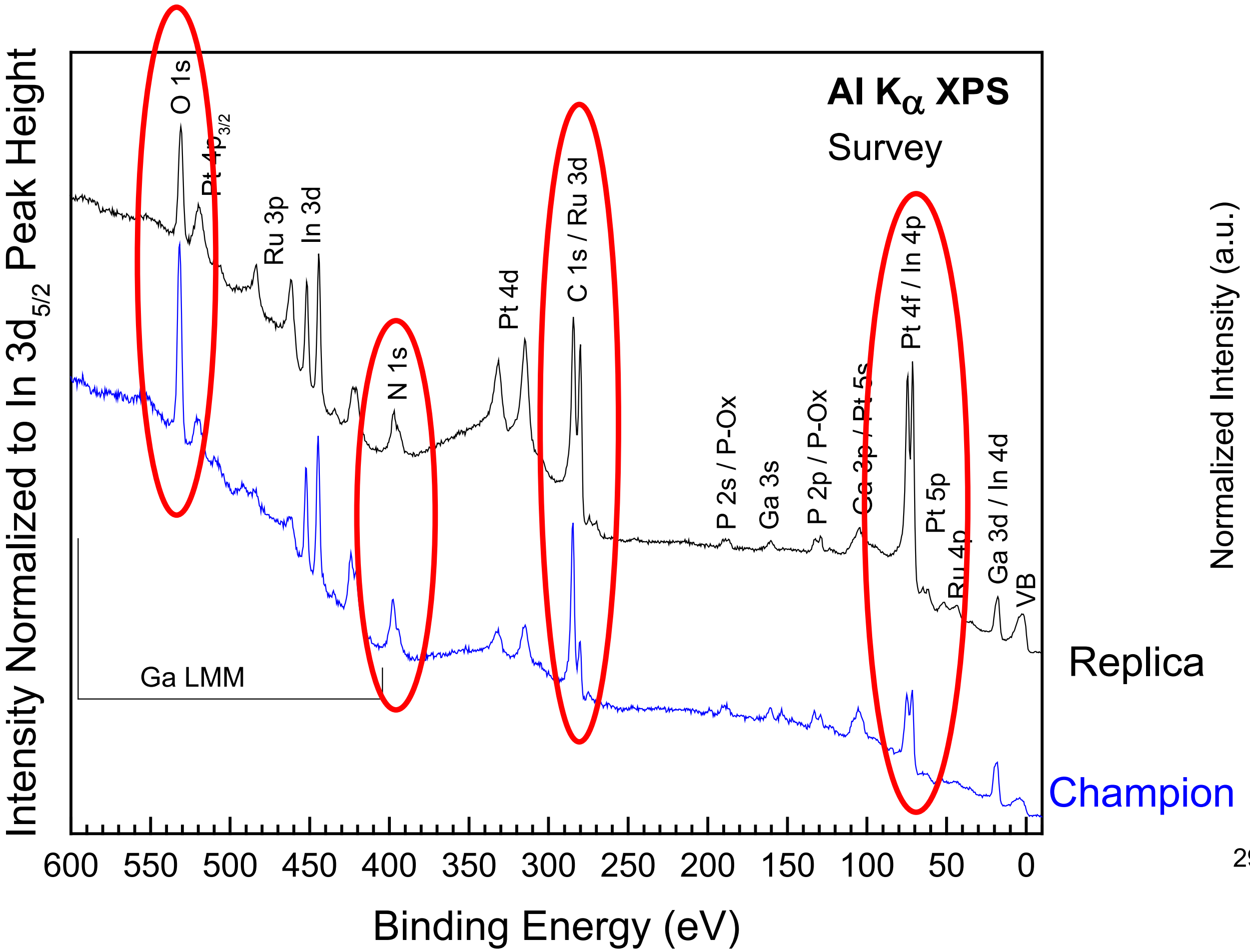
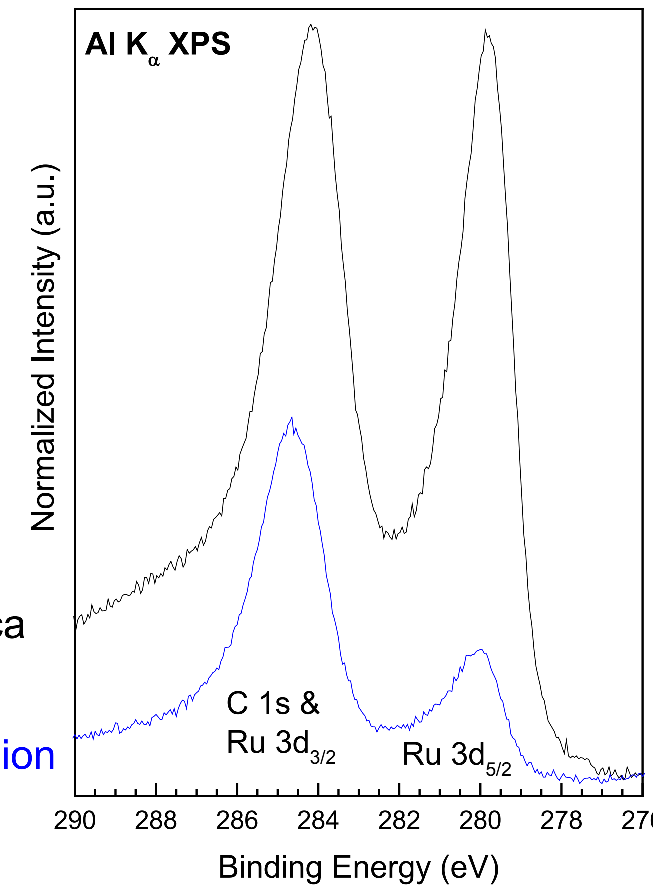
IMM Processing and Photoelectrode Assembly



XPS Comparison – Pt & Ru Loading for Original Champion Sample and Recent "Replication"





Compared to original champion sample, recent replications show

- significantly higher Pt and Ru loading,
- less N at the surface, and
- lower O and C signals due to reduced air-exposure time.

XPS data collection & analysis by UNLV