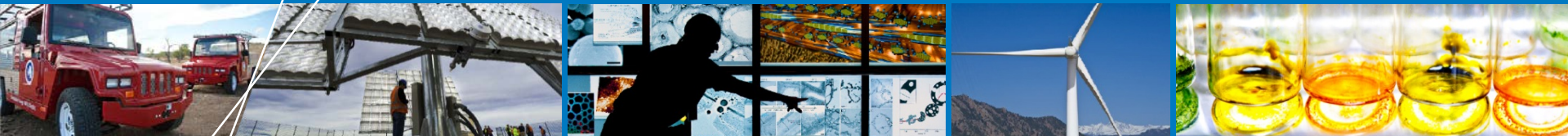


High-Efficiency Tandem Absorbers for Economical Solar Hydrogen Production



**2015 U.S. DOE Hydrogen & Fuel Cells Program
Review**

Todd G. Deutsch

June 11th, 2015

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*: \$0.5M**

* As of 3/31/15

** 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 Oregon
 - Denmark Technical University

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
 - Continue development of stabilizing surface modifications viable at high current densities

Table 3.1.8 Technical Targets: Photoelectrochemical Hydrogen Production: Photoelectrode System with Solar Concentration ^a					
Characteristics	Units	2011	2015	2020	Ultimate Target
		Status	Target	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,1}	%	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

Relevance

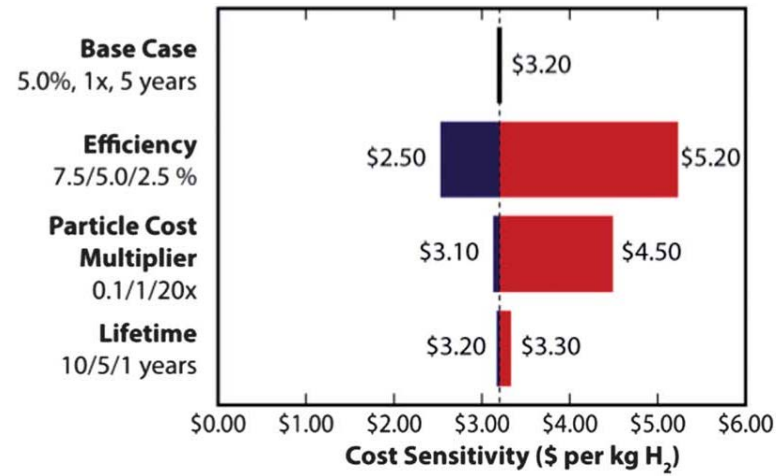
DOE EERE Multi-Year Research, Development, and Demonstration Plan

Table 3.1.8 Technical Targets: Photoelectrochemical Hydrogen Production: Photoelectrode System with Solar Concentration ^a

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

Project Guiding Principles



- Primary focus is on efficiency, the largest lever to reduce H₂ costs according to technoeconomic analysis
- Scalability is primary selection criterion, more important than earth abundance
- Absorber cost and durability (lifetime) issues can be addressed through engineering

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

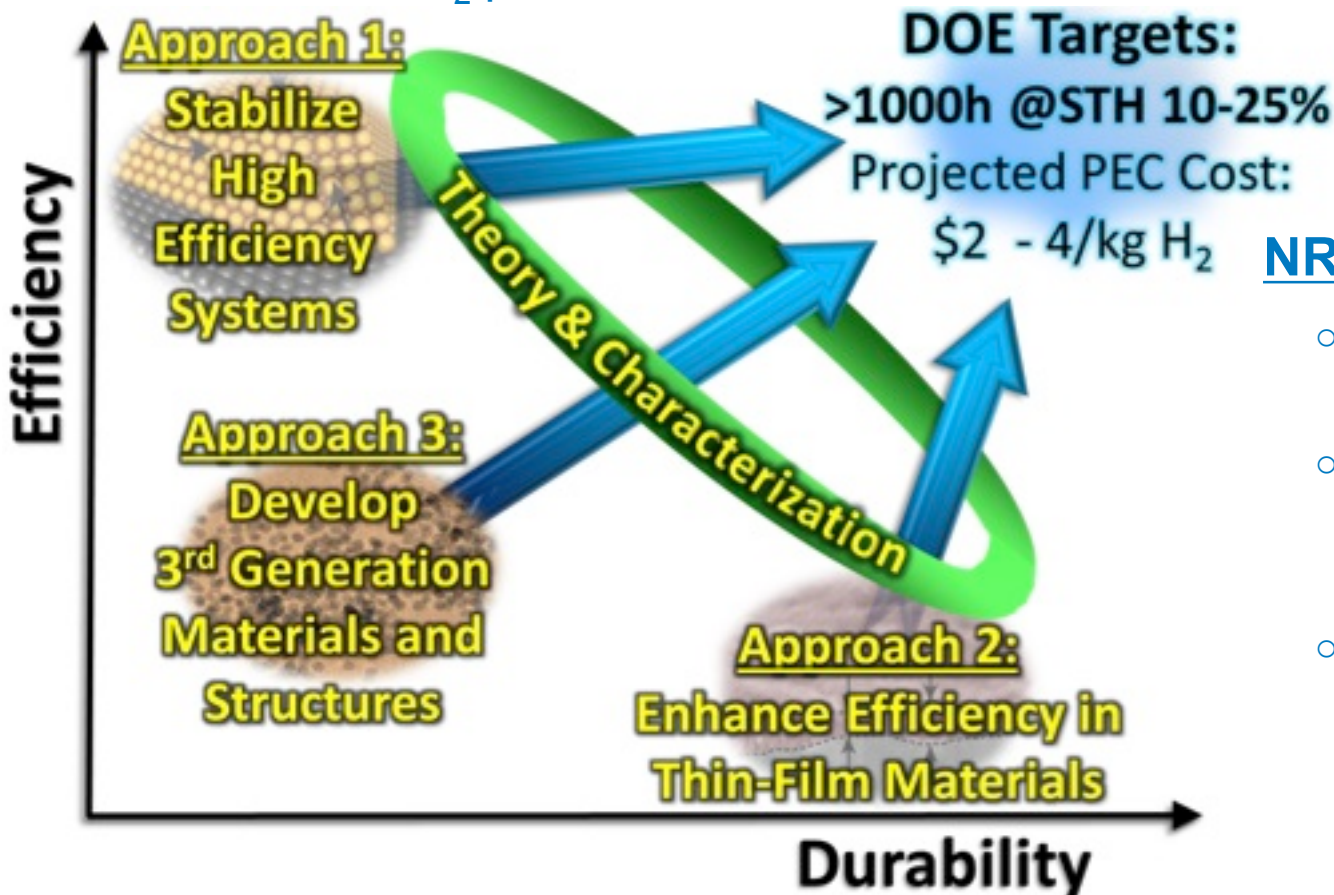
Approach

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 H₂ production



NREL-led Project Focus:

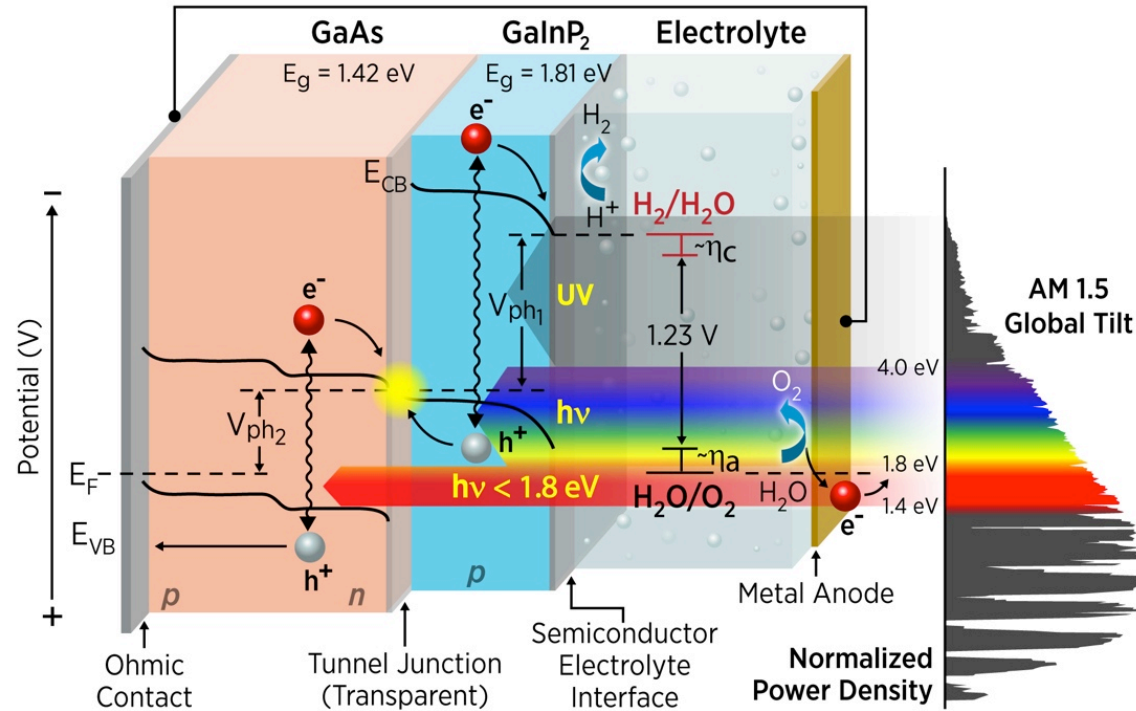
- Extend durability of highly efficient materials
- Ensure efficiencies are not compromised by durability treatments
- Investigate new materials that can achieve ultra-high future efficiency goals

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
 - $\text{In}_x\text{Ga}_{1-x}\text{N}$ tandems (LANL)
 - III-V-N on Si tandems (NREL)
 - Coupled photoanode-photocathode systems (Hawaii, NREL)



• Surface modifications – spectroscopy (UNLV) and modeling (LLNL)

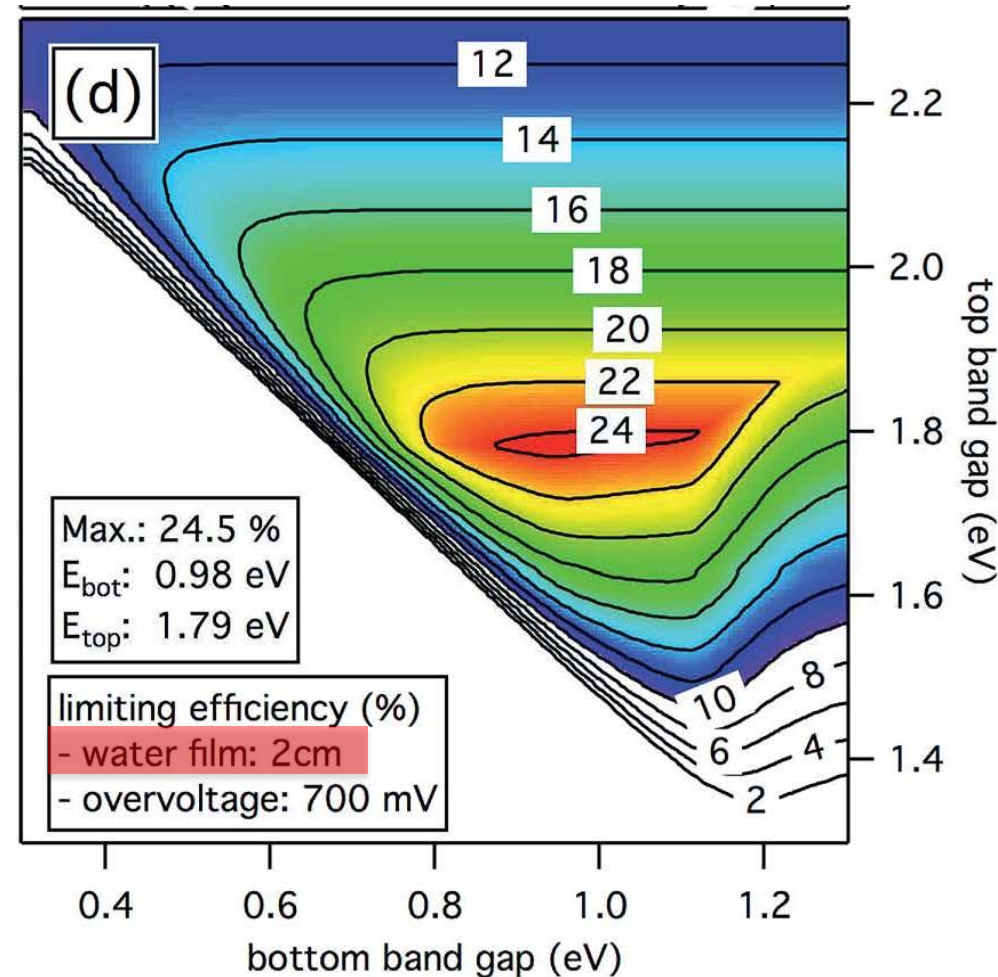
- Ion-implantation & flash sputtering (NREL)
- Thin coatings by atomic layer deposition (NREL, CU)
- Molybdenum disulfide coatings (Stanford)

• Benchmarking, prototyping, & demonstration

- Photoreactor design and outdoor device testing (NREL, JCAP-Solar Fuel Hub)

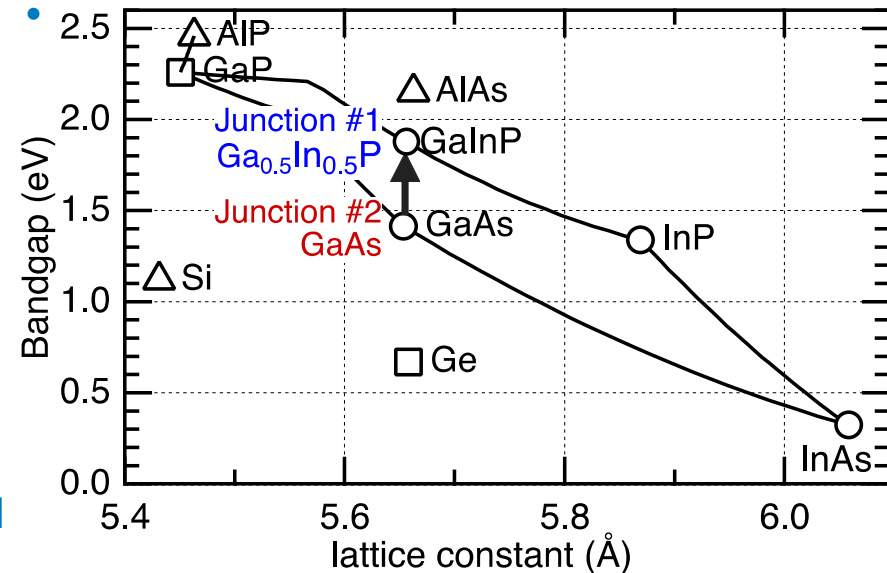
Approach: High Efficiency via Tandems

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



- Exceeding 20% solar-to-hydrogen (STH) feasible
- Reactors with low water penetration for 25% STH
- GaInP₂/GaAs (1.8 eV, 1.4 eV) not optimal

- Traditional MOCVD requires lattice matching from substrate through all epilayers 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

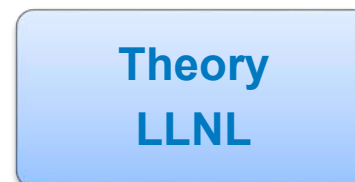
Understanding and remedying semiconductor photocorrosion at PEC interfaces is a complex task that has benefitted significantly from a collaborative approach which teams experts with unique capabilities and resources

- **Heske group at UNLV**

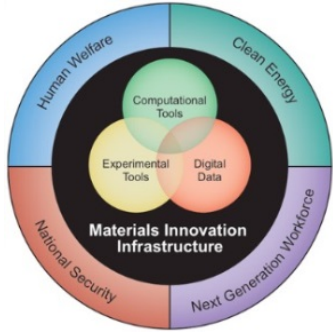
- XPS, XAS, XES, IPES, UPS, AFM
 - Some measurements at Advanced Light Source (ALS)
- Snapshots of surface pre-, intermediate, post-exposure
- Identify common features of and conditions that lead to corrosion
- Characterize stabilized surfaces
 - Show where we are in parameter space wrt. amounts of N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



Advanced Materials Manufacturing (AMM) / Materials Genome initiative (MGI)



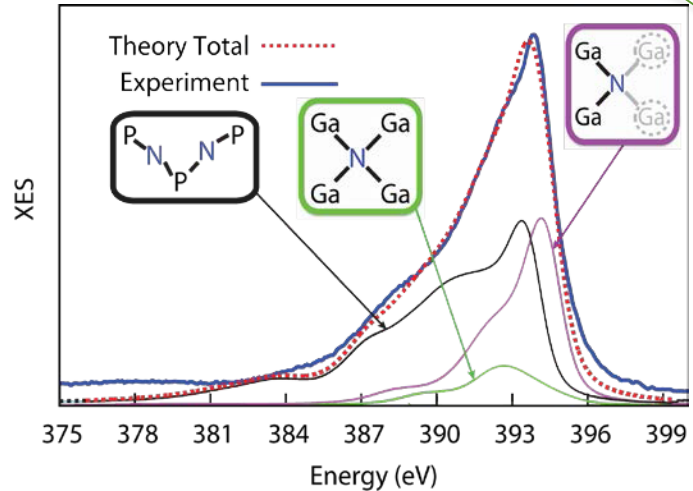
Innovative materials discovery and development for faster product development. Key elements include:

- Integrating experiment, computation, and theory
- Making digital data accessible
- Creating a world-class materials workforce
- Leading a culture shift in materials research

Surface Validation: Photocorrosion of III-V materials with Heske (UNLV), Ogitsu (LLNL)

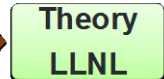
Correlate Spectroscopy with Theory on Nitrided p-GaN₂ System: Establish Base for Predictive Capabilities

- Based on observation that nitridation led to stabilized GaInP₂ surface: Model the *local* nitrogen environment to understand measured spectra
- Theoretical N₂⁺ implanted GaInP₂ nitrogen K-edge XES spectrum by LLNL constructed from various types of nitrogen impurity states as well as the experimental XES measured by UNLV group at LBNL synchrotron



MGI Elements Incorporated: theory, modeling, experimental

- ✓ Encourage and enable integrated R&D
- ✓ Enable creation of accurate, reliable simulations
- ✓ Support creation of accessible materials data repository (sharepoint)
- ✓ Provide opportunities for integrated research experiences



Approach: Pathways to III-V Semiconductor Cost Reductions

- **Optical concentration**
 - 10x-100x uses less absorber
- **Re-use substrate**

NREL report PR-6A00-60126

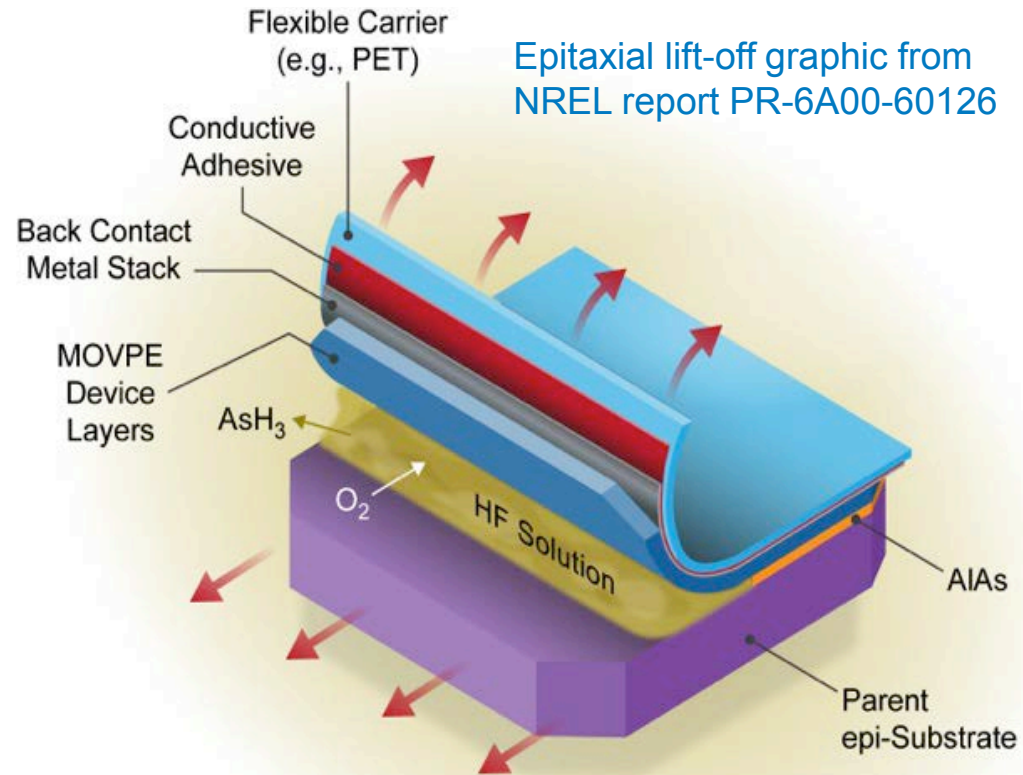
- **Epitaxial lift-off**
 - *Phys. Status Solidi* **202**, 501–508 (2005)
 - **Multilayer epitaxial assemblies**
 - *Appl. Phys. Lett.* **102**, (2013)
 - **Spalling**
 - *Appl. Phys. Lett.* **100**, 053901 (2012)
 - **Laser lift-off**

MRS Comm. 1–5 (2015). doi:10.1557/mrc.2015.2

- **Alternative substrate**

NREL report PR-6A00-60126

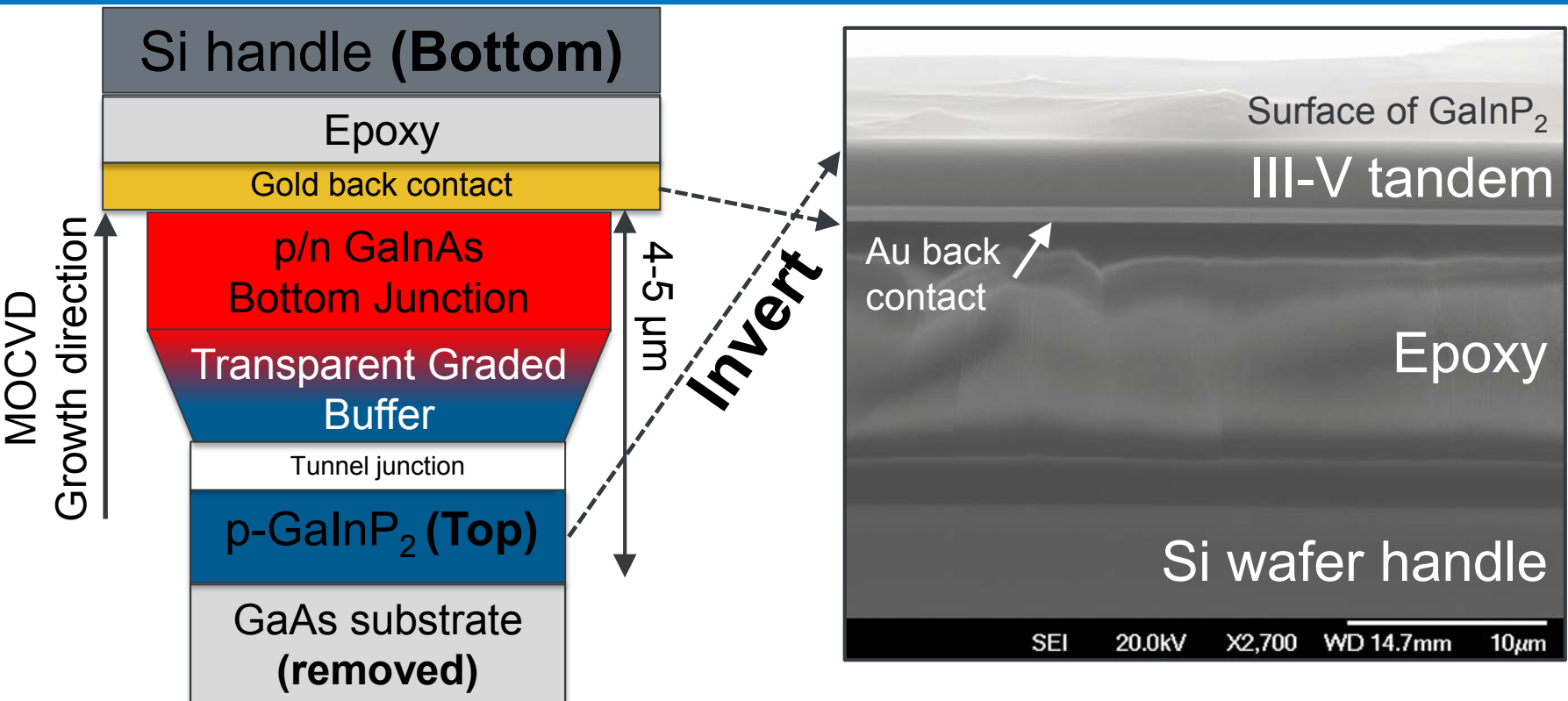
- **III-V on Si**
 - *Semicond. Sci. Technol.* **17**, 769–777 (2002)
- **Metal foil**
 - **Close-space vapor transport**
 - *J. Appl. Phys.* **112**, 123102 (2012)
 - **Ion beam assisted deposition**
 - *Appl. Phys. Lett.* **105**, 092104 (2014)



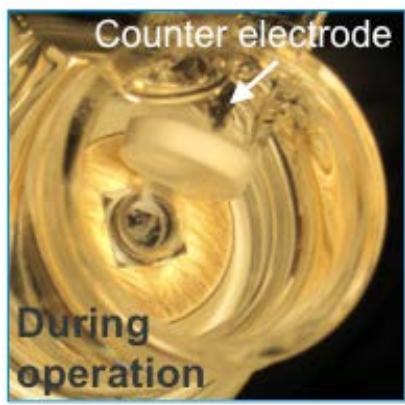
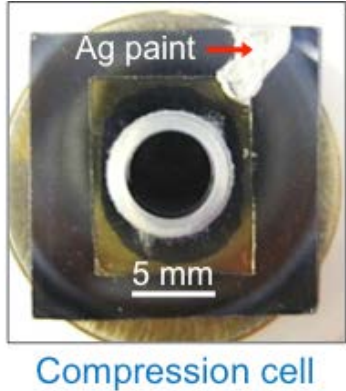
- **Alternative precursors**
 - **Close-spaced vapor transport**
 - *ACS Appl. Mater. Interfaces* **4**, 69–73 (2012)
 - **Hydride vapor phase epitaxy**
 - *J. Appl. Phys.* **113**, 174903 (2013)

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

Progress: Demonstration of IMM for PEC

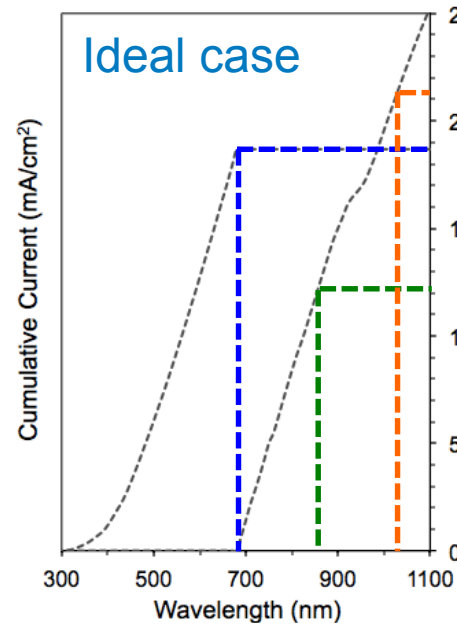
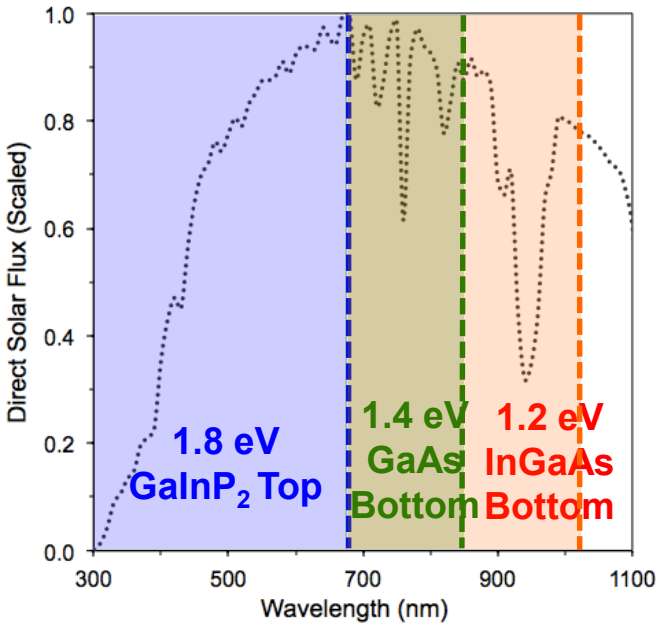


- Inverted growth – light-facing wider bandgap grown first
- Top junction lattice-matched to substrate
 - Device transferred to handle material and substrate removed
 - Potential substrate re-use
 - Reflective back contact



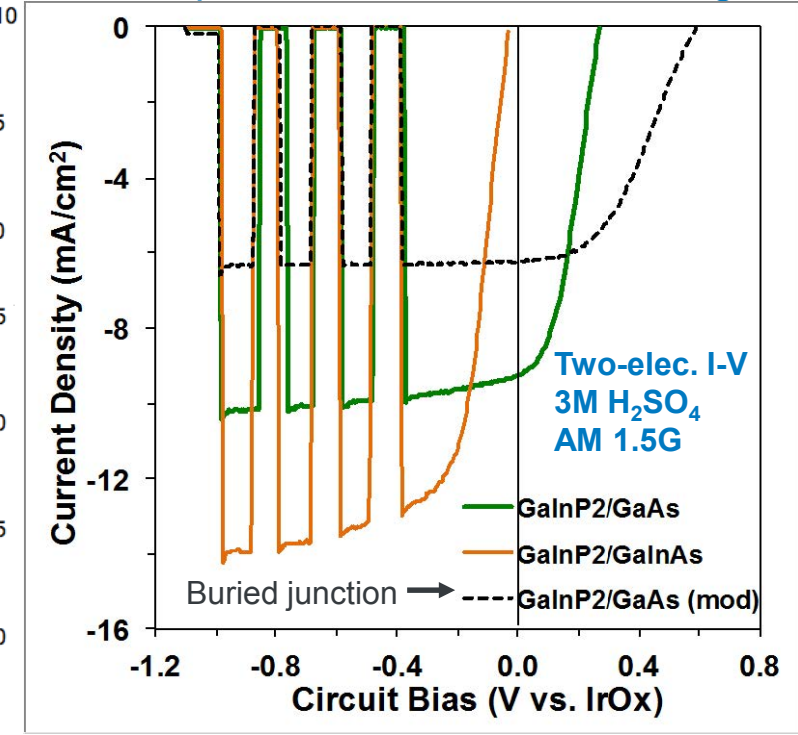
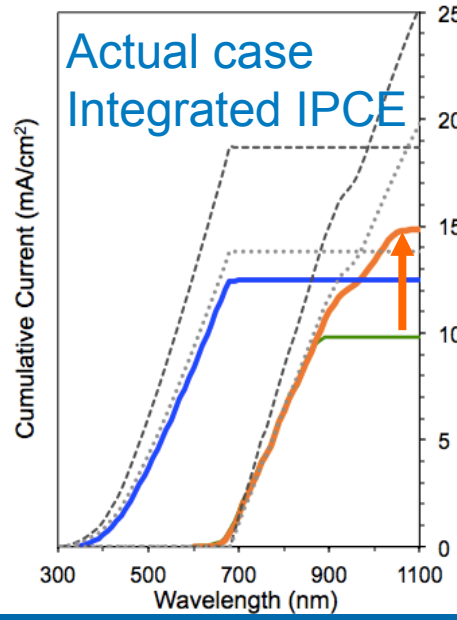
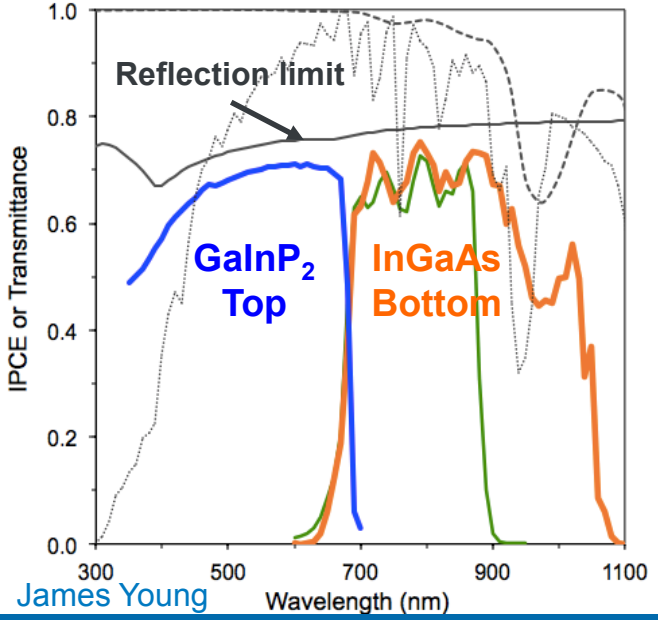
James Young

Progress: IMM Devices for Increased Utilization of Solar Spectrum – On the Path to Higher Efficiency



Increasing bandgap-limited current

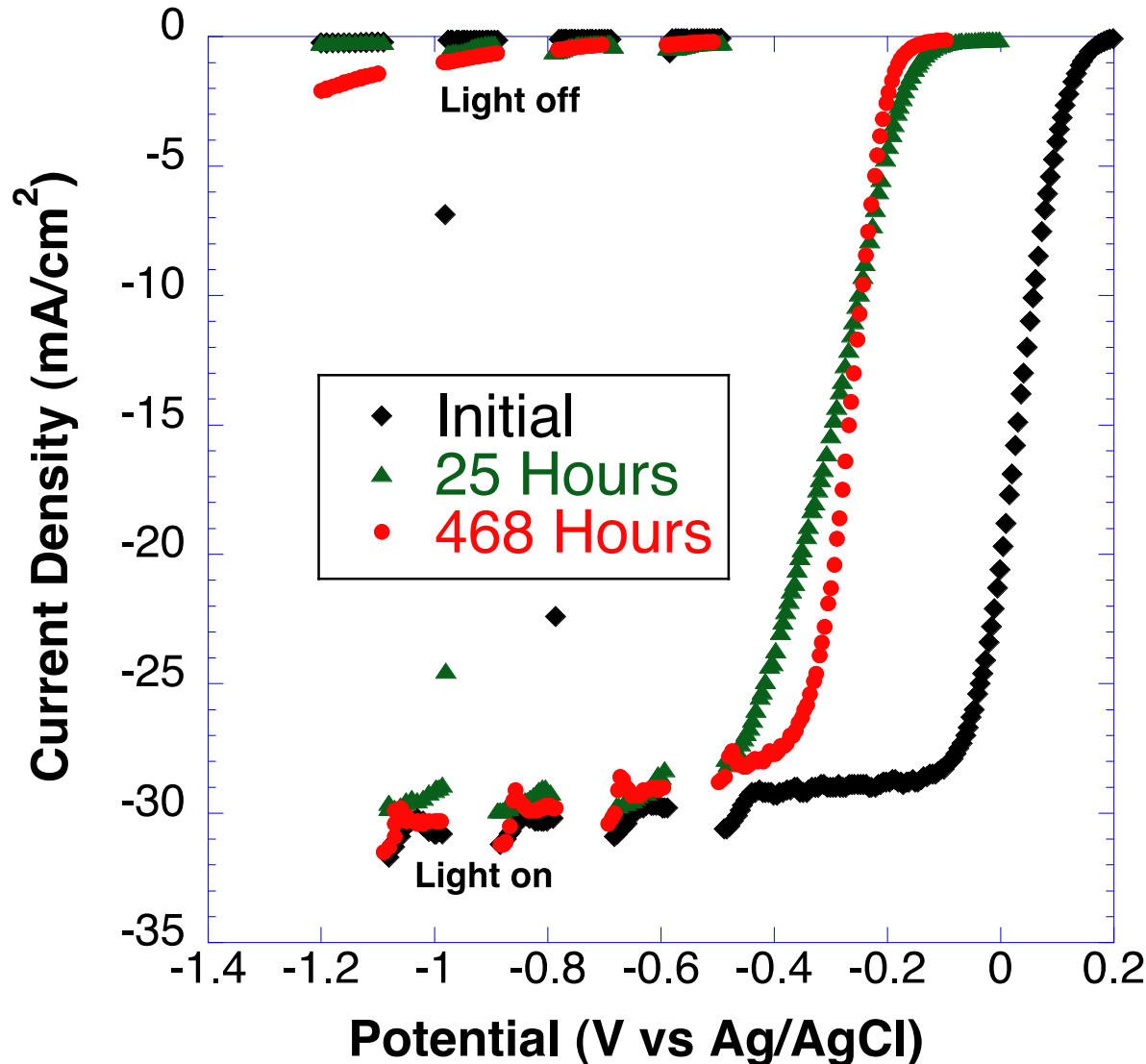
- Absorber junctions in series: voltages add, current limited by lower value (current matching)
- Lowered bottom junction increases total photon flux but lowers voltage



Increased device current
Buried junction to improve voltage
Anti-reflection to smash world-record

Progress: Met 400-hour Milestone – 468 Hours of Durability with N_2^+ /PtRu

Fouling of the electrode was minimized by changing the electrolyte every weekday

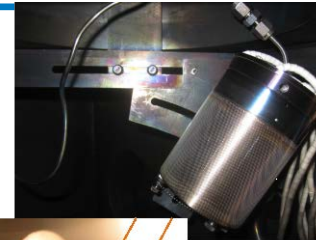


- p-GaAs with N_2^+ ion bombardment and PtRu sputtering
- Operated at $15\text{mA}/\text{cm}^2$ in $3\text{M H}_2\text{SO}_4$ with 1mM Triton X-100
- Some fouling still occurred
- Cleaning in methanol and nitric acid restored light-limited photocurrent to original value
- Photocurrent onset potential was degraded
 - Catalyst deactivation?
 - Catalysts loss?

Over 150 hrs durability with MoS_2
Jaramillo (Stanford) poster PD119

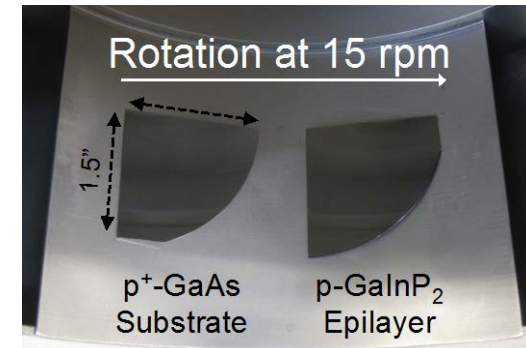
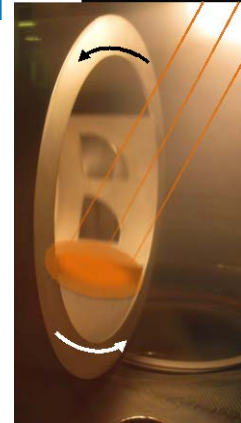
Progress: Mapping Pt & Ru Distribution from N₂⁺/PtRu Surface Modification

- Simultaneously treated GaAs substrate and GaInP₂ epilayers
- Digested entire GaAs wafer, portions of GaInP₂ in aqua regia and Pt, Ru determined by ICP-MS
- Reported in thickness (nm) of compact film
- Results:
 - Nitridation step significant source of PtRu
 - Fairly uniform spatial distribution
 - Full treatment on GaAs much greater than sum of parts



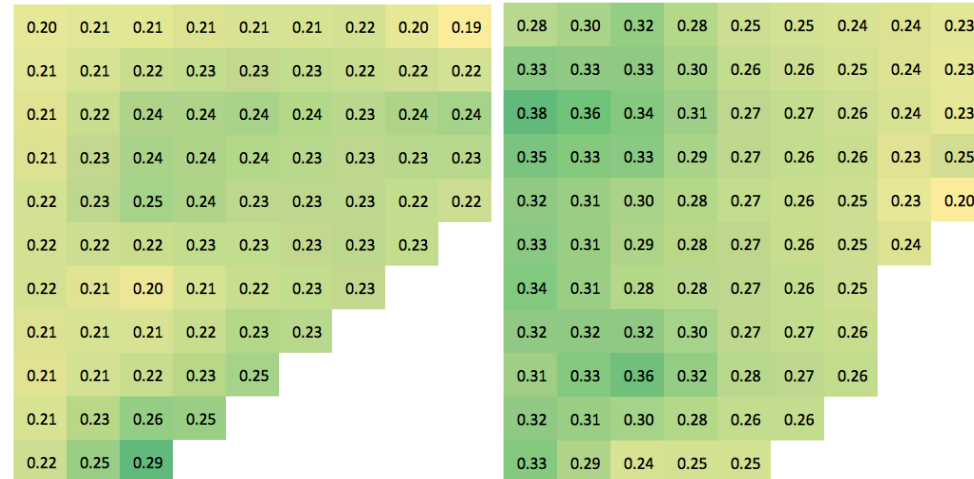
N₂⁺ implantation: 0.7 mTorr N₂, 12 mA beam, 9 minutes @ 15 rpm

PtRu sputtering: 10 mTorr Ar, 20 W DC, 2 rotations @ 15 rpm



Nitridation

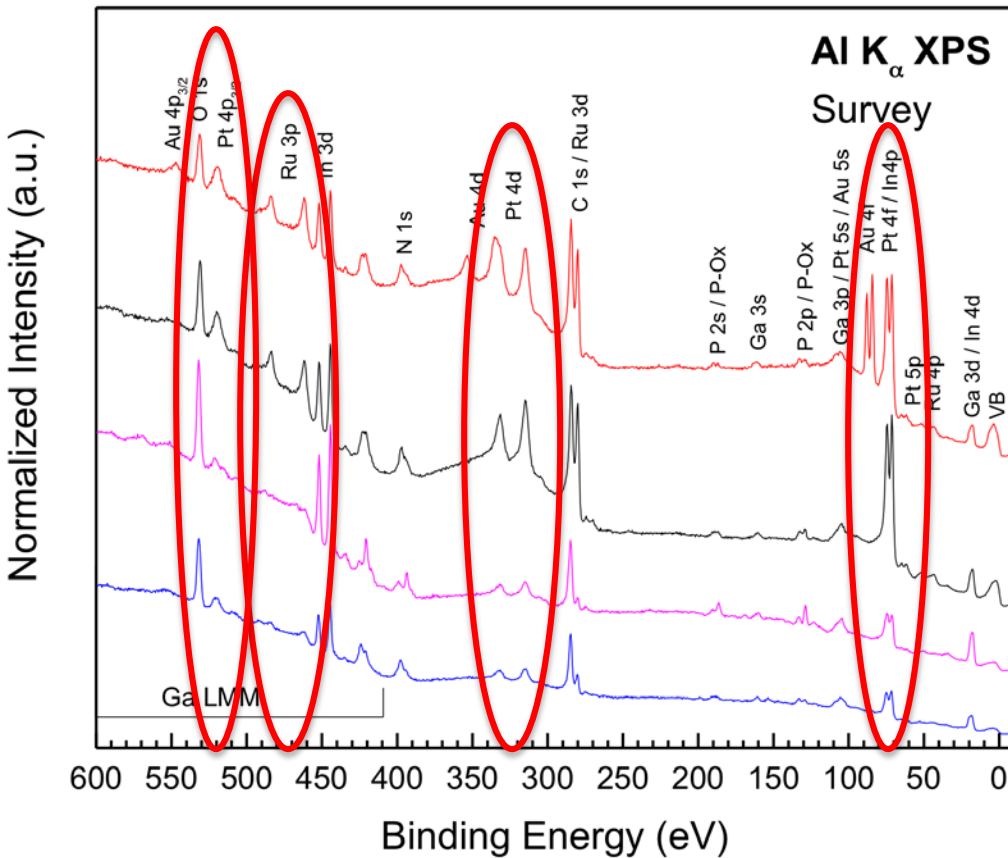
PtRu Sputtering



Ru loading on GaAs (nm)

Treatment	p ⁺ -GaAs Subs. Ru (nm)	p-GaInP ₂ Epi. Ru (nm)	p ⁺ -GaAs Subs. Pt (nm)	p-GaInP ₂ Epi. Pt (nm)
Nitridation	0.22 ±0.02	0.25 ±0.07	0.18 ±0.02	0.19 ±0.06
Sputtering	0.28 ±0.04	0.17 ±0.01	0.19 ±0.02	0.13 ±0.01
Full	1.59 ±0.21	0.44 ±0.07	1.65 ±0.2	0.33 ±0.05

Progress: Work with Surface Validation Partner (UNLV) to Understand PtRu Loading Now vs. Then



Not where we want to be in terms of N and PtRu loading for max durability

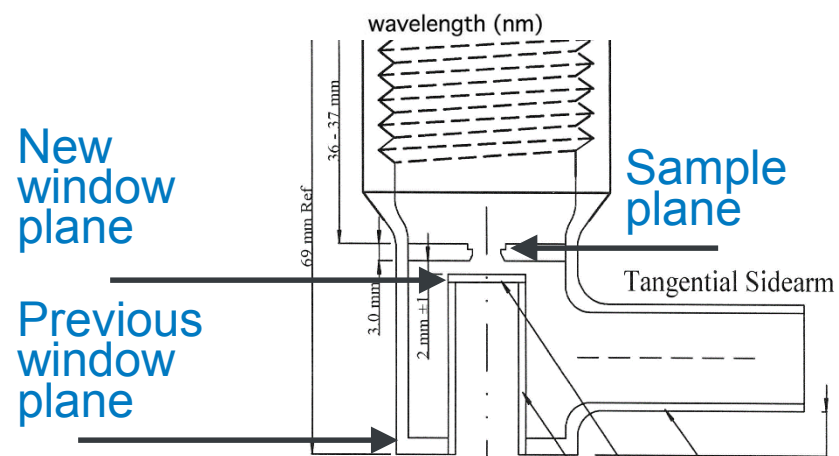
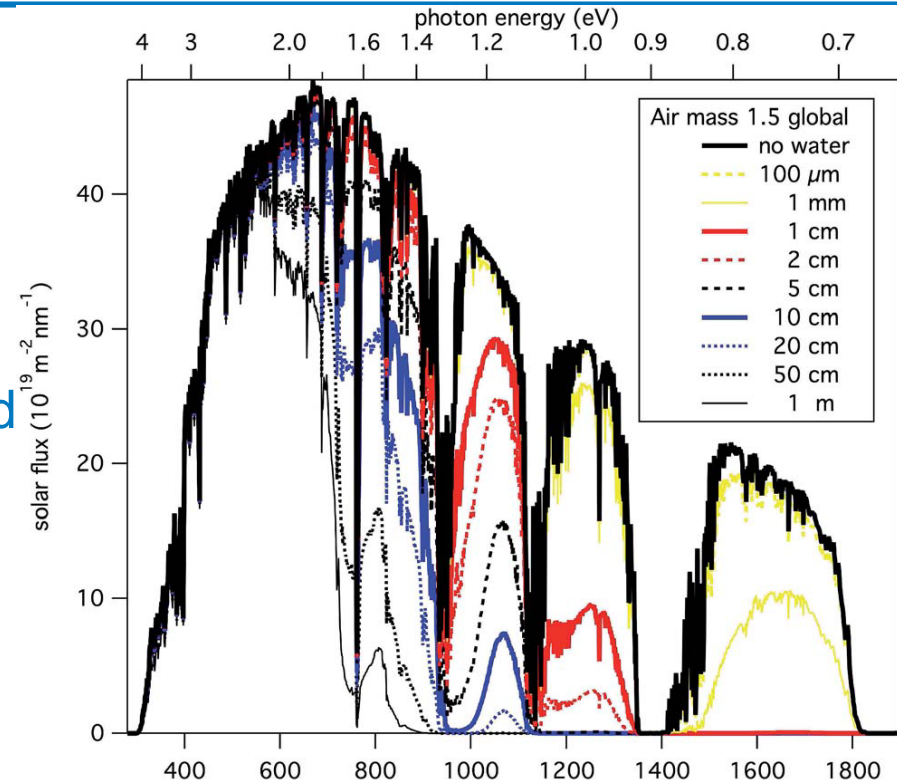
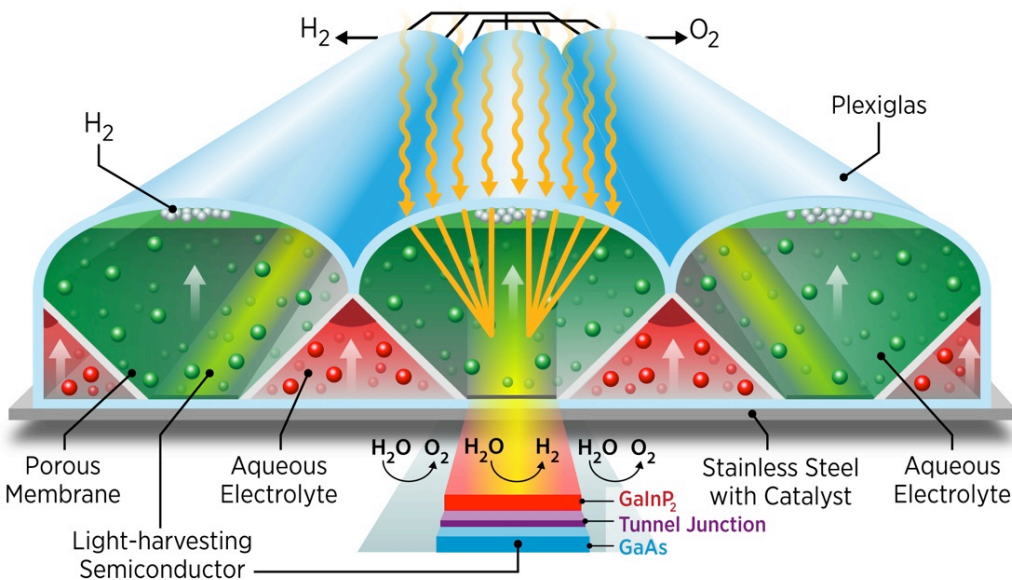
Approximate % of treated GaInP₂ samples with desired durability

New "standard" treatment: (New ion gun, PtRu sputtering)	30%
New "standard" treatment: (New ion gun, PtRu sputtering)	30%
First repetition of protection: (Old ion gun, PtRu sputtering)	90%
Original "magic" sample: (Old ion gun, no sputtering)	90%

- X-ray photoelectron spectroscopy (XPS) by Monika Blum at UNLV reveals significantly (order of magnitude) greater noble metal loading on newer samples
- "Magic" samples had more N (by XES) and less PtRu than current parameter space
- Can't achieve low PtRu and high N with current set-up
- Future: new non-air-exposed samples to UNLV to evaluate N loading & distribution

Progress: Reactor Design

- Initial design had optical concentration from curved front window and large pathlength through electrolyte
- Electrolyte absorbs large fraction of useable infrared photons
- New design for lab characterization and demonstration that reduces electrolyte pathlength from 2 cm to 4 mm



Accomplishments and Progress:

Responses to Previous Year Reviewers' Comments

- **“It is unclear what impact lifetime has on cost projections. A tornado plot would help”**
 - Response: We have included a tornado plot for a type 4 (concentrator) PEC reactor that shows the impact of lifetime on hydrogen cost projections on slide 4.
- **“The singular weakness of this project is the disconnect with the fabrication team for III-V material. It appears the material is produced with a foundry-type relationship. It would be better served if the material fabrication was a more integral part of the project, with shared ownership in the success.”**
 - Response: We have significantly strengthened our interaction with the III-V group in several ways. We wrote in dedicated, direct funding for synthesis in the FOA proposal, we share a postdoc (Henning Döscher) that has expertise in PEC and III-V synthesis that designs and submits run recipes with our input, and we have regular meetings with the III-V group. The enhanced confederation has already borne fruit: the co-inventors on our provisional patent application on IMM III-Vs for photoelectrolysis is a combination of PEC and III-V group members.

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 MoS₂ for stabilization efforts
 - Technische Universität Ilmenau, (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 – DTU hosts one of our students, sample exchange
 - Colorado School of Mines
 - Graduate, postdoc and assistant professor research associates; electron microscopy and XPS user facilities; sample exchange
 - University of Colorado-Boulder
 - Two NSF-graduate research fellow associates under Steve George and Art Nozik are part of our group
 - University of Louisville
 - Sunkara group – novel III-Vs (GaAs_xSb_{1-x})
 - Joint characterizations/publication
 - University of Oregon
 - Boettcher group – Student exchange, joint III-V-N PEC characterizations
 - Helmholtz-Zentrum, Berlin (Germany)
 - Roel Van de Krol – We host student studying transparent OER catalysts

Remaining Challenges and Barriers

- **Efficiency:**
 - Push solar-to-hydrogen efficiency from 12% to beyond 20% for meeting ultimate DOE targets
- **Durability:**
 - Extend our 0.2 year durability to 2 years in the short-term and 10 years long-term
 - More realistic real-world durability assessments
 - Identification and control of non-obvious but stability-relevant process parameters
- **Semiconductor costs:**
 - Reduce synthesis costs by factor of 10 compared to current cost of small-batch III-V materials
- **System testing:**
 - Identify promising photoreactor designs and components
 - Window/body material, sealant/epoxy, membrane, counter electrode

Future Work– Towards *Economical* Hydrogen

In order to achieve the EERE plant-gate, untaxed cost targets of \$1-2/kg H₂ (1kg H₂ = 1gge) requires a PEC system that has 25% solar-to-hydrogen (STH) efficiency, a semiconductor cost around \$150/m², and 10 years of stability.

• Efficiency

- Demonstrate >15% STH efficiency at short circuit for at least 1 hour (milestone)
- Push efficiency by testing lower bandgap configurations that sacrifice voltage to achieve higher currents (efficiencies)

• Durability

- Demonstrate 875 hours of durability at current density equivalent to 15% STH under 1 sun using three surface passivation approaches; work with surface validation team to understand mechanism of protection

• Semiconductor Cost

- Simulate photoreactor performance with higher concentration using multi-physics modeling to evaluate what levels are practically achievable
- Request samples for PEC characterization from others developing innovative III-V synthesis routes being developed by other DOE programs (SunShot, arpa-e)
 - Epitaxial lift-off, spalling, HVPE, CSVT

• Photoreactor Prototyping

- Design and build photoreactors with low optical concentration and low 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 GaInP₂ surface
- Technical Accomplishments:** Developed IMM III-V devices capable of accessing highest possible STH efficiencies, continued optimization of surface treatment conditions and PtRu quantification; GaAs durability – 468 hours of stability @ 15 mA/cm² (improvement on previous 315 hours @ 15 mA/cm²); began collaborative effort with Stanford on MoS₂ protection of III-Vs; modeled absorption of sunlight by water and influence on attainable STH efficiencies – published manuscript and designed new cells based on results; along with UNLV made progress in understanding history of PtRu on GaInP₂
- Collaborations:** Several ongoing, active collaborations with synthesis, modeling, and characterization groups
- Proposed Future Work:** Push STH efficiency limits with IMM III-Vs; evaluate III-V-N/Si tandems for lower cost, higher stability alternative; examine stacked mechanical (dual electrode) tandems with Hawaii; push three surface passivation approaches (N₂⁺/PtRu, MoS₂, ALD TiO₂) to achieve over 875 h durability; design and fabricate concentrator cells and commence regular outdoor testing

Technology Transfer Activities

- **Non-provisional patent filed on nitridation/sputtering surface protection (May 2014)**

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.

- **Provisional patent filed on using inverted metamorphic multi-junction III-Vs to achieve maximum attainable STH efficiency**

Acknowledgements

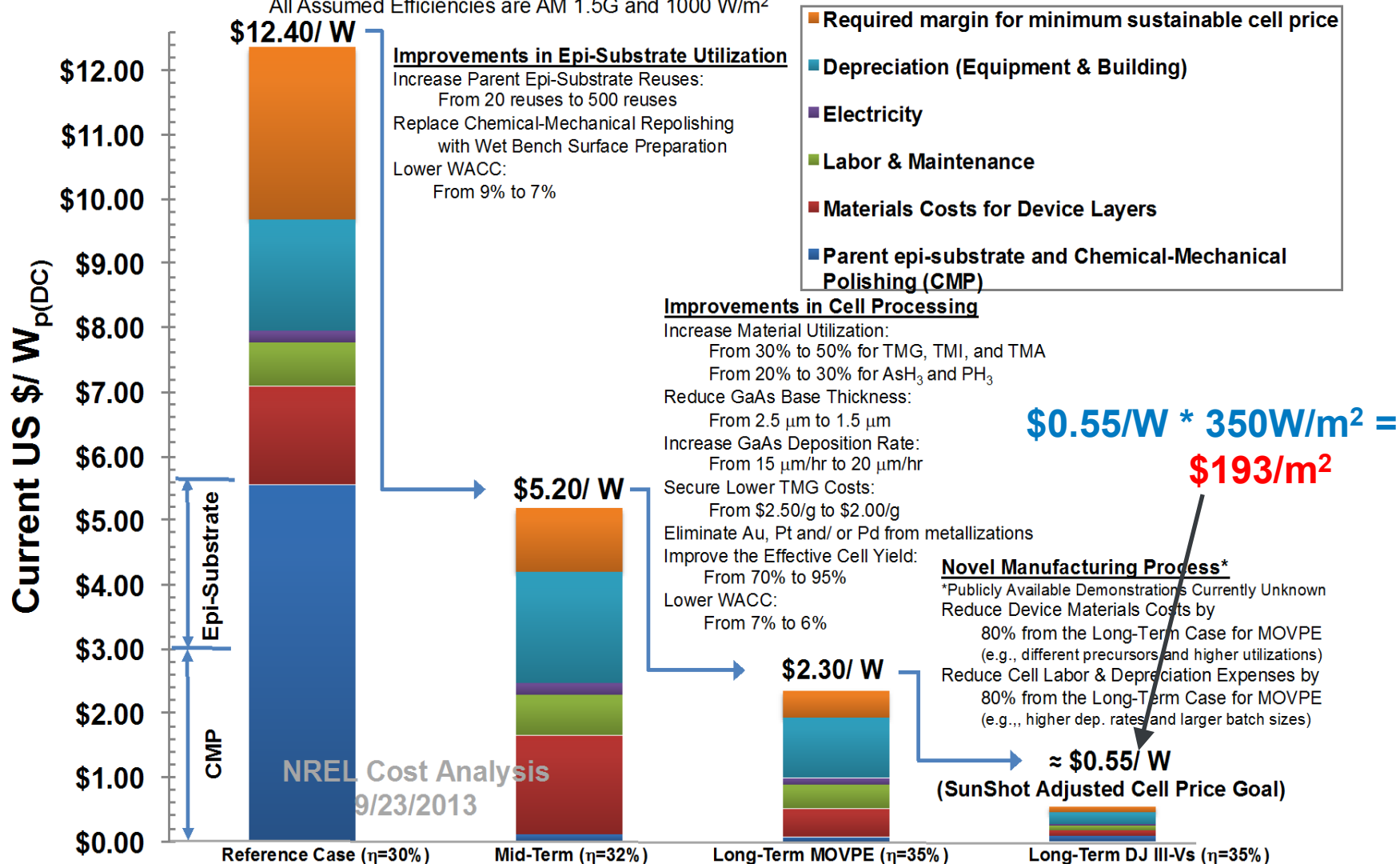
- John Turner – NREL
- Henning Döscher – NREL
- Heli Wang – NREL
- James Young – NREL/CU-Boulder (GS)
- Skye Rios – NREL/CU-Boulder (GS)
- Clay Macomber – NREL
- Huyen Dinh – NREL
- Anna Duda– NREL
- Arrelaine Dameron – NREL
- Andrew Norman – NREL
- All of our amazing collaborators noted throughout this presentation

Technical Back-Up Slides

Cost Model Results for MOVPE of Dual-Junction III-V Solar Cells by ELO

\$150 for 133 cm² Substrates, 400 nm of InGaP on top of GaAs, 500 MW_{P(DC)} U.S. Manufacturing

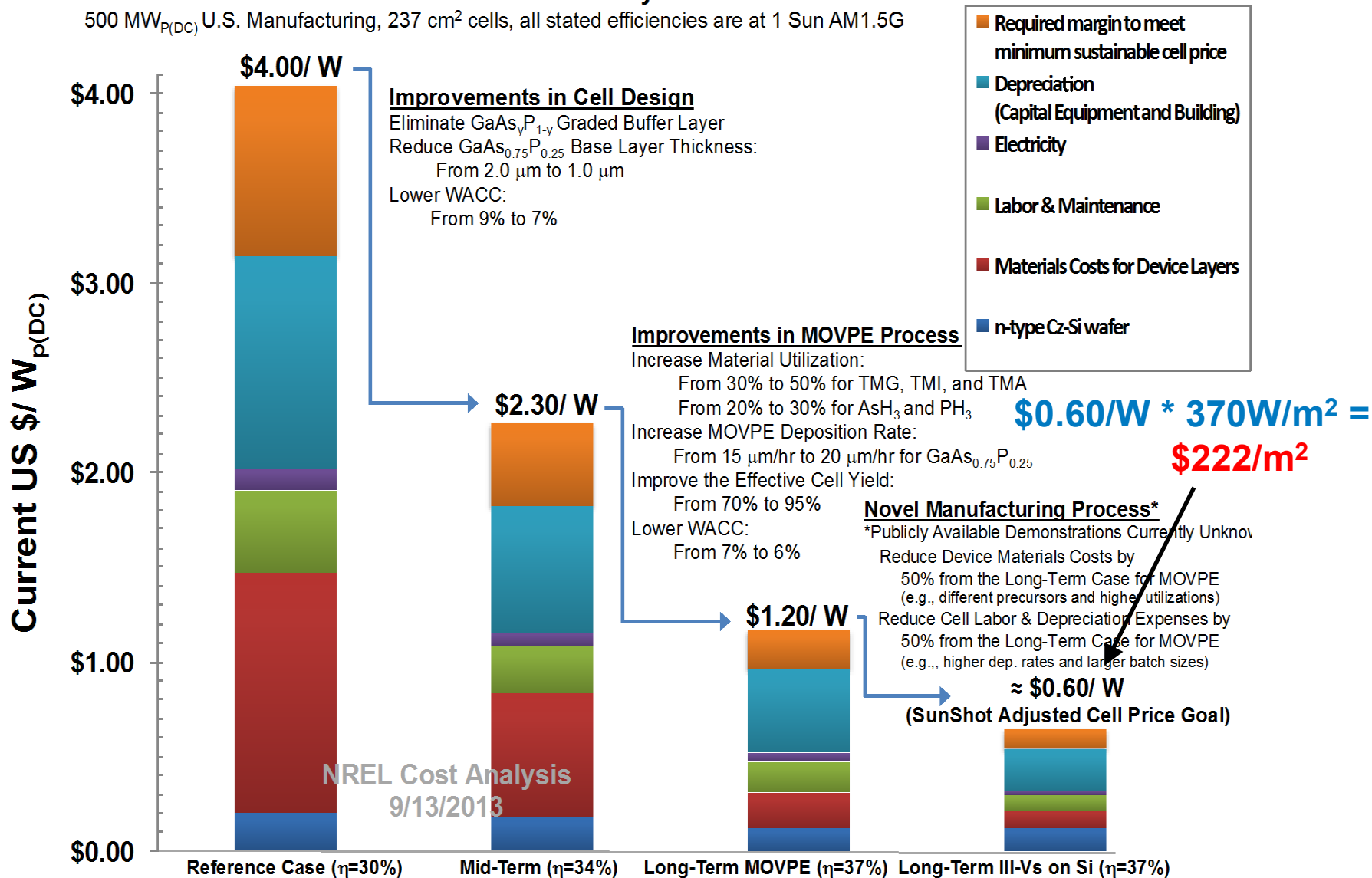
All Assumed Efficiencies are AM 1.5G and 1000 W/m²



Cost modeling projections for high-volume production of dual junction GaInP₂/GaAs PV on GaAs substrates using epitaxial lift-off (ELO) technology for substrate re-use. To get PEC material estimates in \$/m², \$/W is multiplied by 350W/m² (the efficiency). Modeling performed by Mike Woodhouse of NREL's Strategic Analysis group, with funding provided by the DOE SunShot Initiative, "A Manufacturing Cost Analysis Relevant to Single- and Dual-Junction Photovoltaic Cells Fabricated with III-Vs and III-Vs grown on Czochralski Silicon". **Publication Number NREL/PR-6A20-60126**

Cost Model Results for Dual-Junction Solar Cells by MOVPE of III-Vs on Cz-Si

500 MW_{P(DC)} U.S. Manufacturing, 237 cm² cells, all stated efficiencies are at 1 Sun AM1.5G



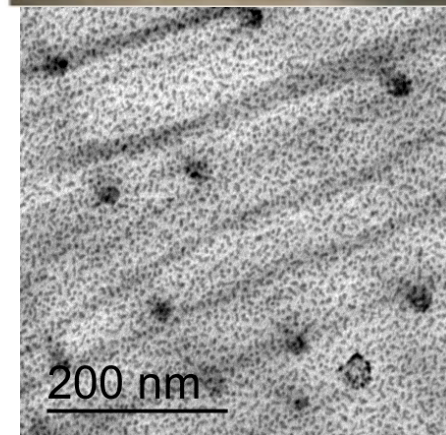
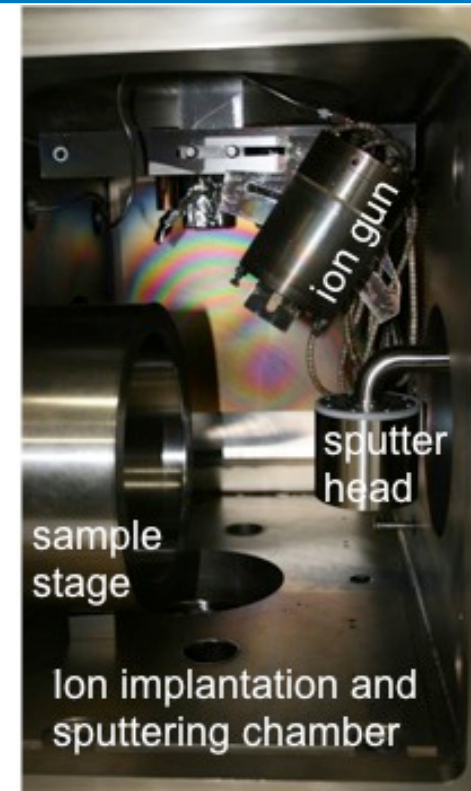
Cost modeling projections for high-volume production of dual junction GaAs_{0.75}P_{0.25}/Si PV on Si substrates. To get PEC material estimates in \$/m², \$/W is multiplied by 370W/m² (the efficiency). Modeling performed by Mike Woodhouse of NREL's Strategic Analysis group, with funding provided by the DOE SunShot Initiative, "A Manufacturing Cost Analysis Relevant to Single- and Dual-Junction Photovoltaic Cells Fabricated with III-Vs and III-Vs grown on Czochralski Silicon". Publication Number NREL/PR-6A20-60126

Details of Ion Implantation and PtRu Sputtering Surface Modification

- Rotating sample stage – 15 rpm
- N_2^+ ion implantation first
 - Key parameters: Angle (55°), distance (20 cm), pressure ($8 \times 10^{-4} N_2$), beam voltage (550 V), beam current (12 mA)
 - Rotated 9 min through ion source (exposed 30 s)
- PtRu alloy sputtering second
 - Two passes through sputter plume (exposed < 0.5 s)

PtRu morphology & loading

- Scanning transmission electron microscopy
 - ~ 5 nm particles with approximately 30% surface coverage
- Inductively coupled plasma mass spectrometry
 - Several samples digested in aqua regia, diluted solutions analyzed for PtRu
 - Equivalent coverage (assuming a continuous thin film) is between 1-2 nm
 - Adds $\$2/m^2$ to absorber costs
 - Requires 66 g of Pt for a 1000 kg/day type 4 reactor array using ultimate DOE targets (25% STH, 15x concentration)



Simulating AM 1.5 G Solar Spectrum

