



# PHOTOELECTROCHEMICAL HYDROGEN PRODUCTION: DOE PEC Working Group Overview & UNLV-SHGR Program Subtask

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**D.O.E Hydrogen Program Review**  
**Arlington, VA**

**#PD35**

*This presentation does not contain any proprietary or confidential information*



# PART ONE

## The US DOE WORKING GROUP ON PHOTOELECTROCHEMICAL (PEC) HYDROGEN PRODUCTION



**Roxanne Garland: Group Chair**  
*U.S. Department of Energy*

**Eric Lars Miller: Group Co-Chair**  
*University of Hawaii at Manoa*

The DOE PEC Working Group is a collaborative effort between Academic, Industry and National Laboratory leaders to research and develop semiconductor systems for photoelectrochemical (PEC) hydrogen-production. Working Group Members with current DOE financial support include:



- *University of Hawaii at Manoa*
- *University of Nevada Las Vegas*
- *University of Toledo*
- *University of California, Santa Barbara*
- *University of Nevada Reno*
- *Caltech University*
- *Stanford University*
- *Colorado State University*
- *National Renewable Energy Laboratory*
- *Intematix Corporation*
- *MVSsystems Incorporated*
- *Midwest Optoelectronics*

# OBJECTIVES *PEC WORKING GROUP*

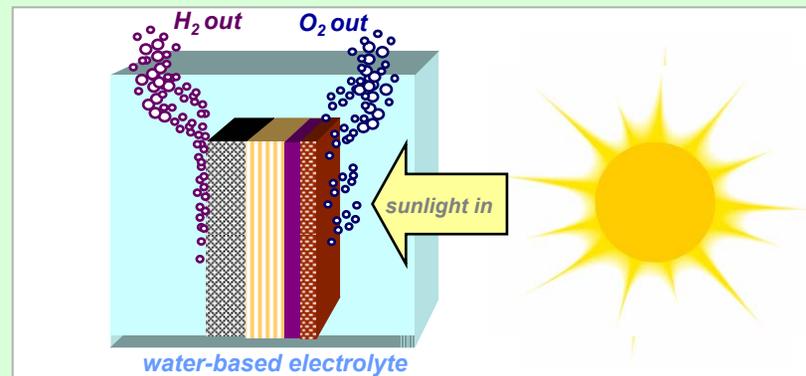
The DOE PEC Working Group's primary objective is to develop practical solar hydrogen-production technology, using innovative semiconductor materials & devices R&D to foster the needed scientific breakthroughs

## *DOE PEC Program Targets*

**Table 3.1.10. Technical Targets: Photoelectrochemical Hydrogen Production<sup>a</sup>**

Characteristics	Units	2003 Status	2006 Status	2013 Target	2018 Target <sup>b</sup>
Usable semiconductor bandgap <sup>c</sup>	eV	2.8	2.8	2.3	2.0
Chemical conversion process efficiency (EC) <sup>d</sup>	%	4	4	10	12
Plant solar-to-hydrogen efficiency (STH) <sup>e</sup>	%	not available	not available	8	10
Plant durability <sup>f</sup>	hr	not available	not available	1000	5000

***photoelectrode-based  
PEC solar-H<sub>2</sub> production:  
must out-perform PV/electrolysis***



# <sup>5</sup>THE PEC CHALLENGE PEC WORKING GROUP

**NO** Material System satisfies **ALL** requirements to efficiently split  $\text{H}_2\text{O}$ ...  
Many have potential... **Thus the PROMISE & CHALLENGE of PEC**

## ➤ ABSORBER MATERIAL

- Sunlight conversion depends on bulk optical bandgap
- Nature of optical transitions ('direct' vs. 'indirect') is important
- Good bulk transport properties key to harnessing photo-carriers

## ➤ INTERFACE DESIGN

- Band-edge alignment important to reaction energetics
- Surface bandgap plays an important role at interface
- Interface kinetics critical in harnessing photo-carriers

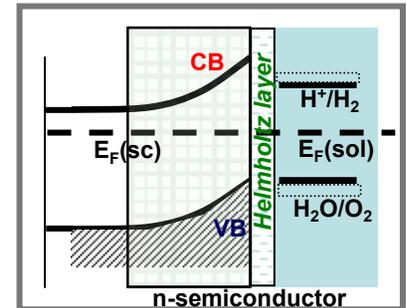
## ➤ INTEGRATED DEVICE DEVELOPMENT

- Multi-junction configurations important for maximum solar utilization
- Auxiliary components and proper integration key to efficiency

## ➤ HYDROGEN PRODUCTION SYSTEM DEVELOPMENT

- Balance of plant considerations could limit practicality

## ➤ COST



# APPROACH *PEC WORKING GROUP*

The main approach of our collaborative network of world-leaders in materials R&D focuses on integrating state-of-the-art theoretical, synthesis and analytical techniques to identify and develop the most promising materials classes to meet the PEC challenges in efficiency, stability and cost.

## ➤ *The PEC Materials R&D Feedback Loop*



### THEORY: Materials & Interface Modeling

–Theoretical Calculations of Semiconductor Band Structures

### SYNTHESIS: Materials Discovery / Development

–Physical and Chemical Vapor Deposition

–Combinatorial & Manufacture-Scale Synthesis Techniques

### ANALYSIS: Materials & Device Characterization

–Physical/Solid-State Electronic/Optoelectronic Properties

–Solid-Solid & Solid-Liquid Interface Characteristics

–Photoelectrochemical Behavior Analysis

➤ ***Continue to Develop the PEC “Tool-Chest”, and to Apply to the Selection and R&D of the Most Promising Focus Materials & Systems, including:***

- ***Metal Oxides ( $WO_3$ ,  $Fe_2O_3$ ,  $TiO_2$ ,  $ZnO$ , etc.)***
- ***Mixed-Metal Oxides (CoFeAl Spinel, etc.)***
- ***Group III-V Semiconductors***
- ***Amorphous Silicon-Compound Semiconductors***
- ***Copper Chalcopyrite Alloy Semiconductors***
- ***Metal Nitrides, Oxinitrides, and Sulfides***
- ***Mixed-Semiconductor, Multi-junction Systems***

# **KEY ACTIVITIES** *PEC WORKING GROUP*

- **Supporting the development of theoretical, synthesis, and characterization tools vital to the R&D of PEC materials, interfaces, devices and systems**
- **Supporting group-member research activities to develop PEC materials, interfaces, devices and systems**
- **Developing standardized PEC materials and device measurement protocols essential to research validation**
- **Developing the up- and down-selection criteria for viable PEC materials systems critical to prioritizing research resources**
- **Initiating “Techno-Economic” analyses of the practical viability of PEC solar-hydrogen production plants**
- **Expanding collaborative research both nationally and internationally (*e.g., coordinated PEC research with IEA, IPHE..*)**

# PART TWO

## The DOE UNLV-SHGR PROGRAM: PEC SUBTASK



**Robert Perret: Project Manager**

*University of Nevada Las Vegas Research Foundation*



*SHGR PEC subtask collaborators*

## Timeline

- Project start date: 1 Oct. 2004
- Project end date: 31 Oct. 2008
- Percent complete: 85%

## Barriers

- Barriers for photoelectrochemical hydrogen production technologies:
  - Y: *Materials Efficiency*
  - Z: *Materials Durability*
  - AB: *Bulk Materials Synthesis*
  - AC: *Device Configuration Designs*

## Budget

- Total project funding: \$2.84M
  - DOE share: \$2.12M
  - Contractor share: \$721k
- FY06 Funding : \$ 958k
- Funding for FY07: \$0
  - No-cost extension to 10/31/08

## Collaborators / PIs

- University of Hawaii at Manoa/ Eric L. Miller
- University of Nevada, Las Vegas/ Clemens Heske
- University of California, Santa Barbara/ Eric McFarland
- MVSystems Incorporated/ Arun Madan
- Intematix Corporation/ Xiaodong Xiang
- Altair Nanotechnologies Incorporated/ Vesco Manev
- National Renewable Energy Laboratory/ John Turner & Mowafak Al-Jassim



# OBJECTIVES *DOE-SHGR PEC*

- Identify and develop PEC thin-film materials systems compatible with high-efficiency, low-cost H<sub>2</sub> production devices:
  - Target Range: 1.6 – 6.5 mA/cm<sup>2</sup> AM 1.5 PEC photocurrent (with 100-1000 hour durability)
- Demonstrate functional multi-junction device incorporating best-available PEC film materials:
  - Target Range: 2 - 8 % STH conversion efficiency (AM 1.5)
- Develop collaborative avenues (national and international), integrating the best theoretical, synthesis and analytical techniques, for optimizing future PEC materials and devices
- Explore avenues toward manufacture-scaled devices and systems

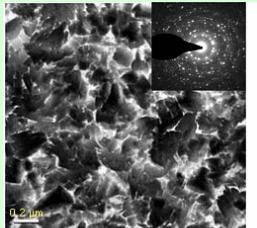
# APPROACH *DOE-SHGR PEC*

## ➤ *Develop & Refine the PEC “TOOL-CHEST”:*



- **THEORY:** Materials & Interface Modeling
- **SYNTHESIS:** Materials Discovery / Development
- **ANALYSIS:** Materials & Device Characterization

## ➤ *Apply to the Development of Focus Materials Classes:*



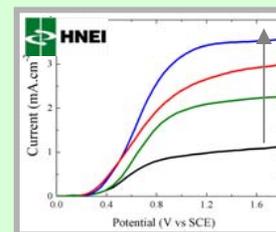
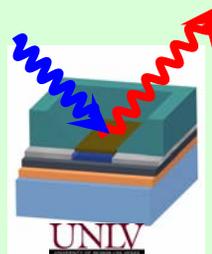
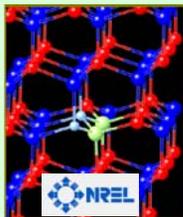
Highly crystalline  $\text{WO}_3$



- **TUNGSTEN** -Based Compounds
- **SILICON**-Based Compounds
- **COPPER-CHALCOPYRITE** Compounds
- **ZINC-OXIDE** -Based Compounds
- **IRON-OXIDE** -Based Compounds
- Others (outside of SHGR umbrella)

# PROGRESS OVERVIEW *DOE-SHGR PEC*

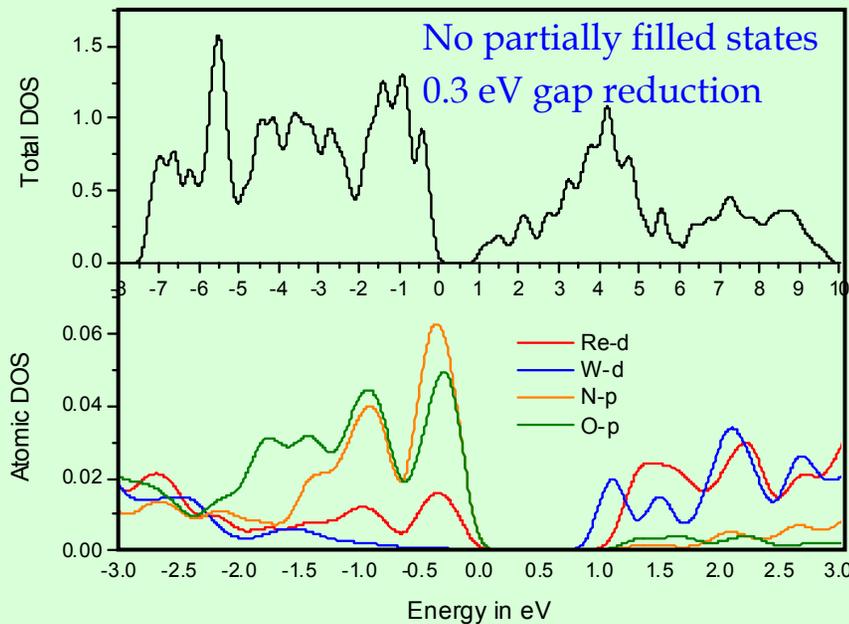
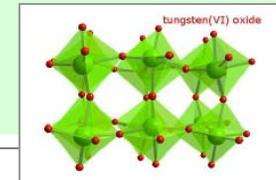
- Important Advances in PEC Materials Theory
- Expansion of PEC Materials Synthesis Techniques
- Continued Progress in PEC Materials Characterizations
- Successful Application of New “Tool-Chest” Capabilities
- Significant Results in Focus Materials Classes
- Further Expansion of Collaborative Research Efforts
- Avenues Developed for Continued Research Funding



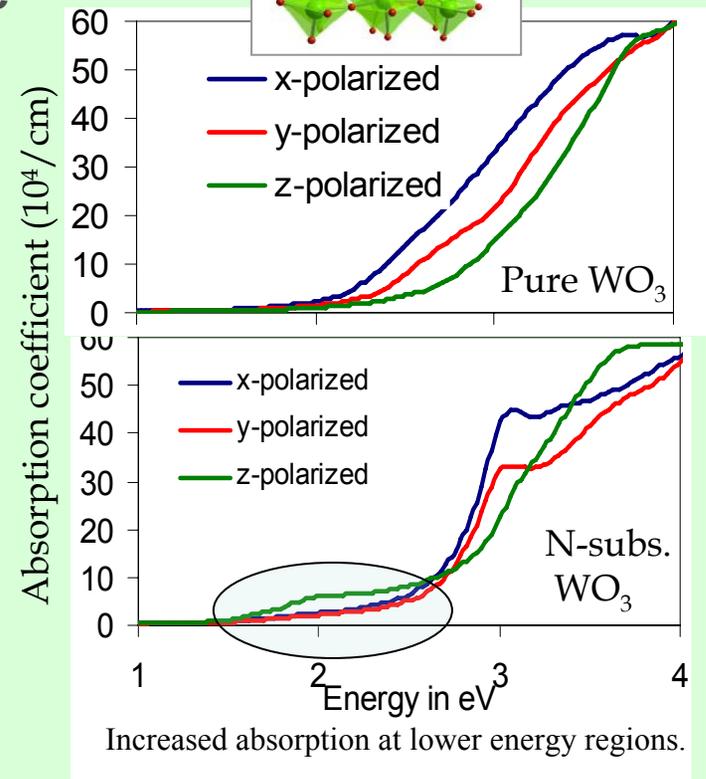
## WO<sub>3</sub> Systems

*theory provides invaluable guidance in tungsten-based materials*

- Band gap and positions can be modified by doping
- Co-incorporation can enhance performance



Re-N co-doping reduces recombination



## Density Functional theory study of metal-oxides: Band engineering for better PEC

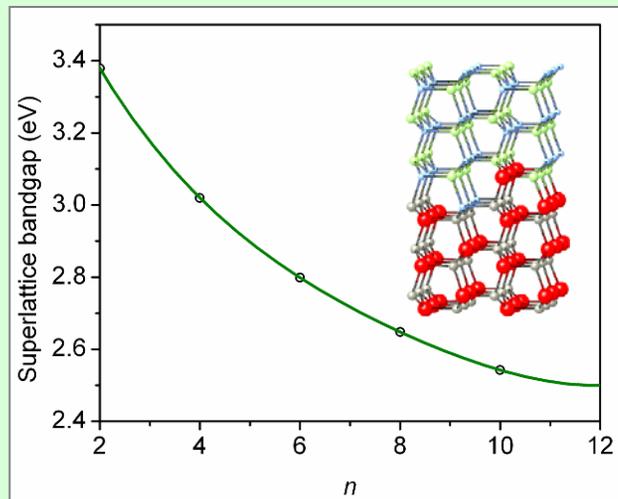
### ZnO:GaN Systems

*theory provides general guidance in synthesis of mixed-metal oxides*

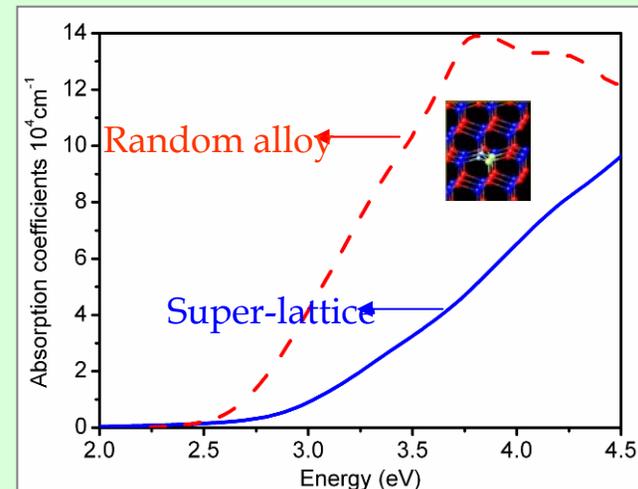
- ZnO-GaN results in reduced band gap
- Band gap reduction is asymmetric
- ZnO is a better host than GaN
- Random alloy system is more effective than the super-lattice system

Host	Eg reduction
Ga-N in ZnO	0.410
Zn-O in GaN	0.102

ZnO is a better host than GaN for Eg reduction



n, number of ZnO (or GaN) layer

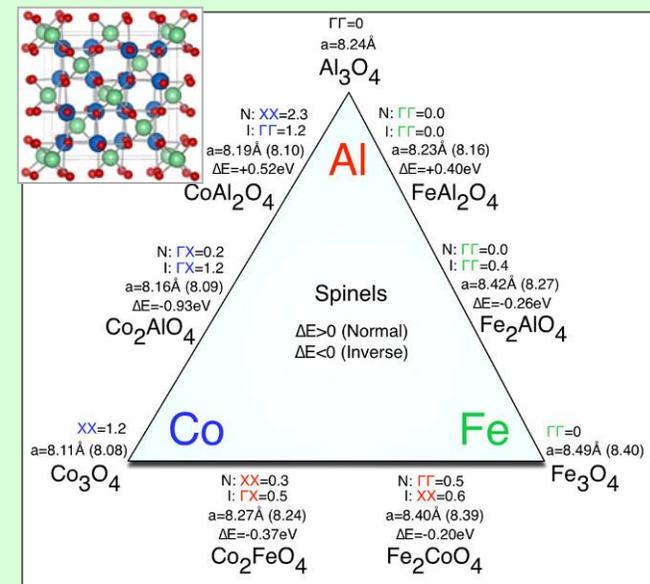


Calculated total absorption coefficient spectra

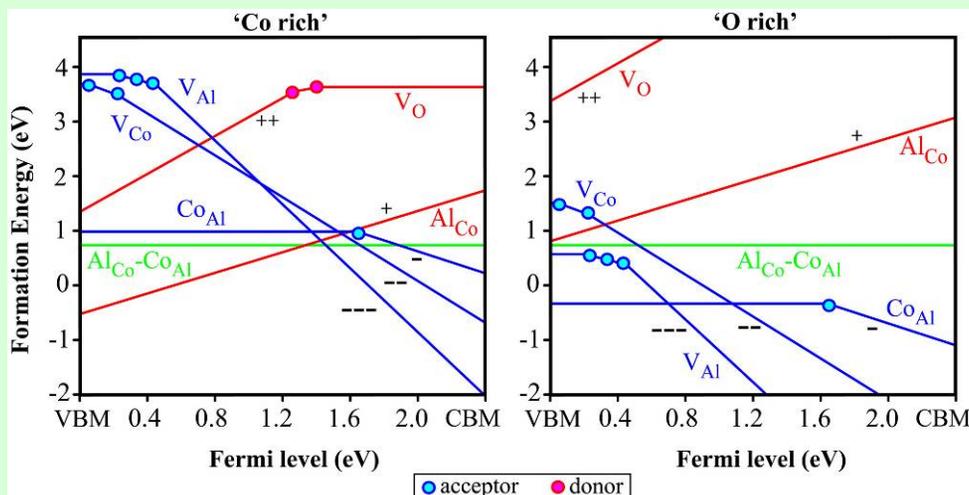
## Co-Fe-Al Spinel Systems

powerful theoretical to identify new promising mixed-metal oxide systems

- Calculation of structural, magnetic and electronic properties of nine binary and ternary spinel oxides formed from Co, Al and Fe
- Examination of energetics of possible intrinsic point defects and Fe-doping in spinel  $\text{CoAl}_2\text{O}_4$  and their effect on its electronic & chemical properties



(Above) Summary of the calculated structural and electronic properties of the three binary and six ternary Co-Fe-Al spinels.



(Left) Calculated intrinsic defect formation energies as a function of the Fermi level under Co rich and O rich conditions

# Theory Advances DOE-SHGR PEC

Future work can be guided by “Theoretical Combinatorial Discovery”

		Ry	eV		VBM(Ry)	eV	CBM (Ry)	Gap (eV)		
ZnO	O-1s	-36.88521	-501.639		0.253161	3.442992	<b>1.8918(eV)</b>	0.8		
CuAlO <sub>2</sub>	O-1s	-36.72122	-499.409		0.479977	6.527694	0.626988448	<b>1.999349281</b>	indirect	<b>with WIEN2k</b>
CuYO <sub>2</sub>	O-1s	-36.77843	-500.187		0.349289	4.750336	0.541505768	<b>2.614142472</b>	direct	
CuMnO <sub>2</sub>	O-1s	-36.84509	-501.093							metallic compound
<b>CuWO<sub>4</sub></b>	<b>O-1s</b>	<b>-36.69258</b>	<b>-499.019</b>		<b>0.489023</b>	<b>6.650707</b>	<b>0.668499565</b>	<b>2.440887114</b>	indirect	Not delafossite
YTaO <sub>4</sub>	O-1s	36.573963	497.4059		0.490876	6.675919	<b>0.769877542</b>	3.794415934	indirect	
YVO <sub>4</sub>	O-1s									
YNbO <sub>4</sub>	O-1s									metallic compound
<p><b>CuBO<sub>2</sub>, CuAlO<sub>2</sub>, CuScO<sub>2</sub>, CuYO<sub>2</sub>, CuLaO<sub>2</sub>, CuEuO<sub>2</sub>, CuMnO<sub>2</sub>, CuWO<sub>4</sub>, YTaO<sub>4</sub>, YVO<sub>4</sub>, YNbO<sub>4</sub>, ZnV<sub>2</sub>O<sub>4</sub>, ZnMn<sub>2</sub>O<sub>4</sub>, ZnCr<sub>2</sub>O<sub>4</sub>, ZnTiO<sub>2</sub>.</b></p>										
<p><b>Theoretically main obstacle is to calculate band-offset. And, of-course, the old band-gap problem.</b></p>										
ZnO	O-1s									
ZnV <sub>2</sub> O <sub>4</sub>	O-1s									by VASP
ZnMn <sub>2</sub> O <sub>4</sub>	O-1s	502.56950	3.95310	1.1467		4.3949	4.1815	<b>0.44180</b>	<b>3.03480</b>	highly
ZnCr <sub>2</sub> O <sub>4</sub>	O-1s	502.04410	4.41400	2.0396		6.0512	5.6225	<b>1.63720</b>	<b>3.58290</b>	magnetic

# Diverse Synthesis Routes DOE-SHGR PEC

The SHGR team commands a broad portfolio of thin film synthesis techniques to facilitate the discovery and development of PEC materials and devices—including a range of advanced techniques for rapid discovery of new materials classes and the establishment of large-scale device fabrication...

- Physical Vapor Deposition Systems
- Chemical Vapor Deposition Systems
- Spray Pyrolysis Fabrication Systems
- Sol-Gel Fabrication Systems
- Combinatorial Synthesis Systems
- Manufacture-Scale Film Technology



*Reactive sputtering system for compound material films*



*Automated combinatorial physical-vapor-deposition system*



*Cluster tool for vacuum-deposition of manufacture scale thin-film devices*



*Co-Evaporation system for copper chalcopyrite films*

- **Significant Development of Instrumentation Systems**
- **Progress in Establishing Standard Testing Protocols**
- **Significant Advances in Understanding of PEC Materials**

**Test Protocols:** *Experiment Complexity: (I) standard experiment, (II) medium complexity, (III) high*

## Characterization of Materials Properties

Morphology: Scanning Electron Microscopy (II), Atomic Force Microscopy (II), Spectroscopic Ellipsometry (I)

Microstructure: X-Ray Diffractometry (I), Electron Backscattered Diffraction (II), Transmission Electron Microscopy (II)

Chemistry: Secondary Ion Mass Spectrometry (II), X-ray Photoelectron Spectroscopy (II), X-ray Emission Spectroscopy (Synchrotron) (III), X-ray Absorption Spectroscopy (Synchrotron) (III), Energy-Dispersive X-ray Analysis (II)

## Characterization of the Electronic Structure

(Electronic Surface Band Gap, Band Edges, Band Alignment, Fermi Energy, Work Function, Electrical Properties)

UV Photoelectron Spectroscopy (II), Inverse Photoemission (III), Impedance Spectroscopy (I), UV-Vis Spectroscopy (I), Conductive Atomic Force Microscopy (III), Scanning Kelvin Probe Microscopy (III), Scanning Tunneling Microscopy/Spectroscopy (III)

## Characterization of Optical and Photoelectrochemical Properties

Optical-Photoelectrochemical Combinatorial Screening (II), Diffuse Reflectance Spectroscopy (I), Solar Cell I-V Curve Testing (I), Solar Cell Spectral Response Measurement (I), Incident Photon to Current Efficiency (IPCE) (II), Photoluminescence (II), Cathodoluminescence (II)



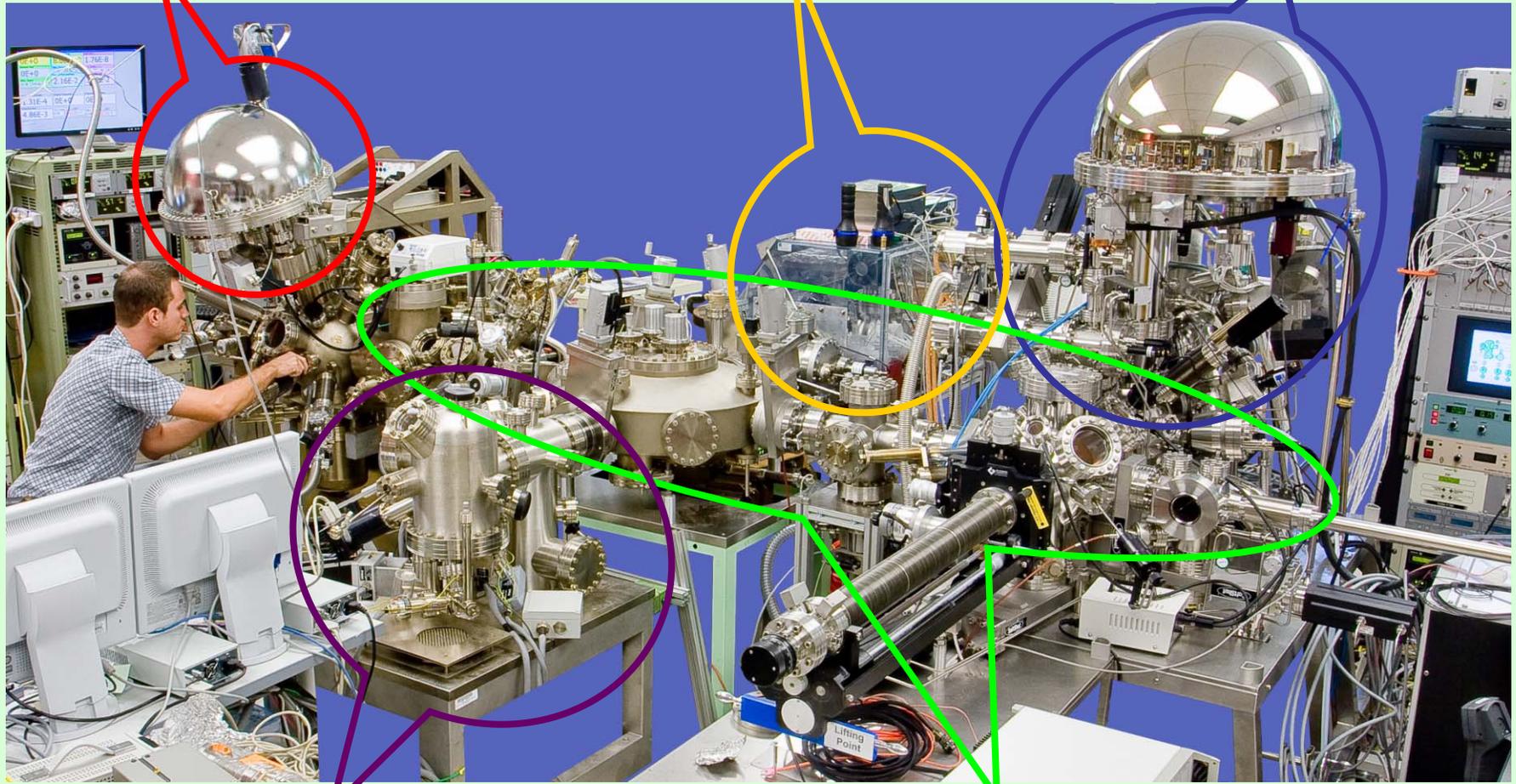
# Characterization Progress

DOE-SHGR PEC

High dynamic range  
XPS, UPS, Auger, IPES

Glovebox

High resolution  
XPS, UPS, Auger

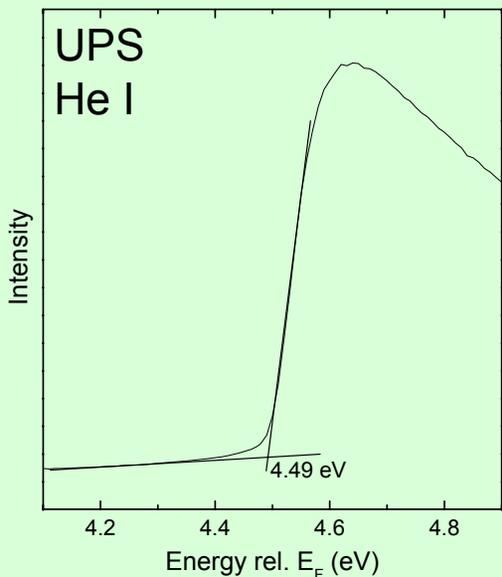
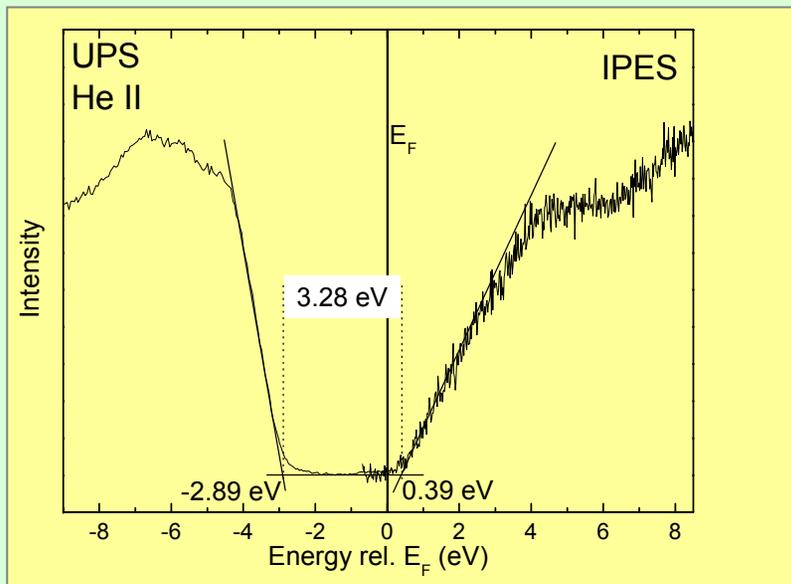


Scanning Probe  
Microscope

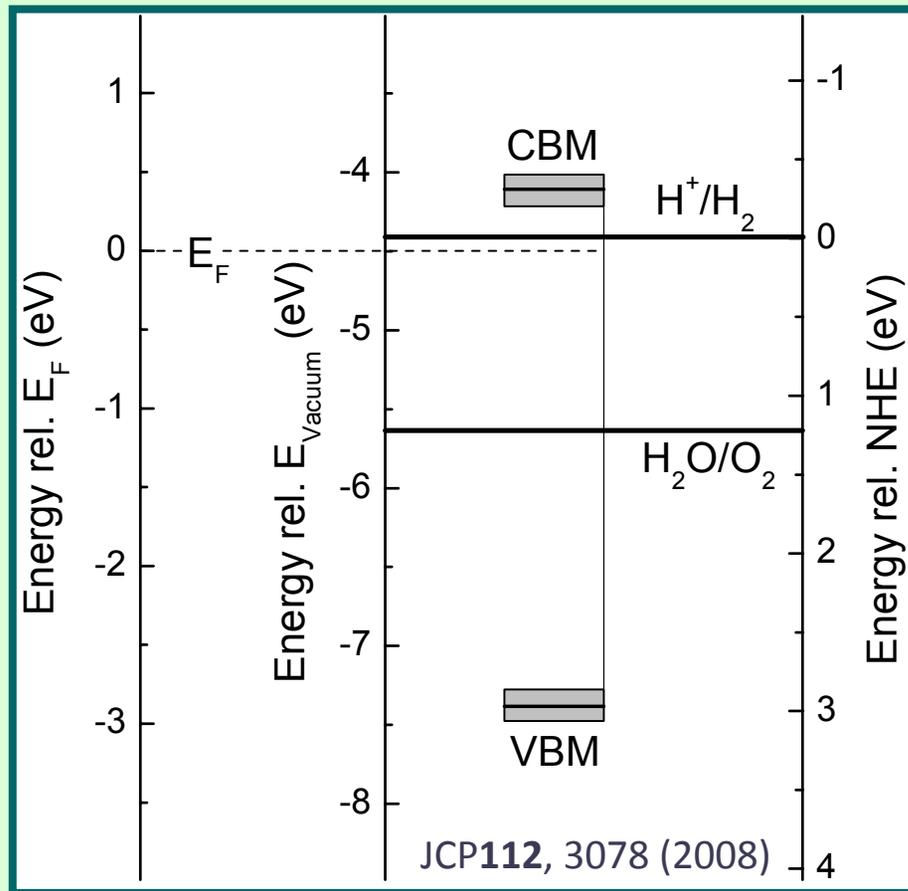


Sample preparation and  
distribution

First all-experimental depiction of the  $\text{WO}_3$  surface electronic structure

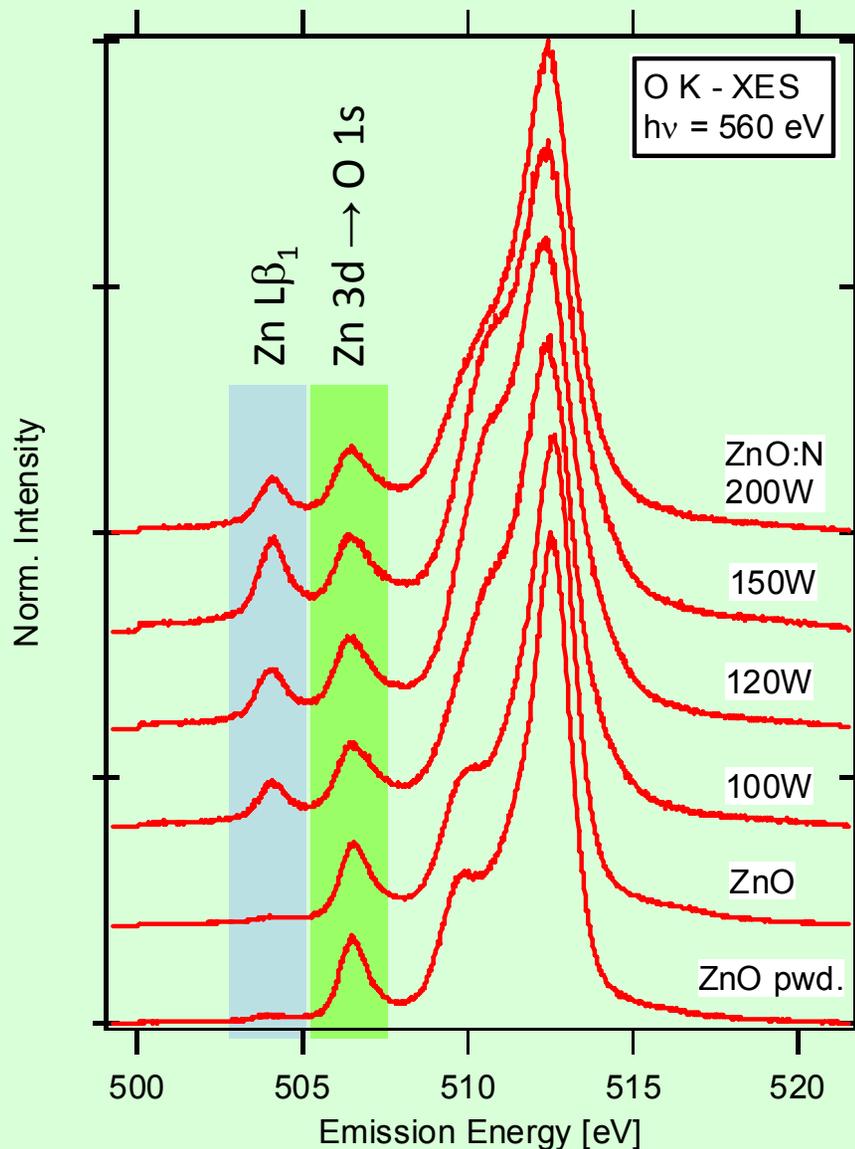


Combining  
direct and  
inverse  
photoelectron  
spectroscopy



➤ Invaluable asset in understand of material surface electronic states

## ZnO:N – Stoichiometry Determination with X-ray Emission Spectroscopy



Using the O K emission to determine the  $Zn_3N_2/(ZnO+Zn_3N_2)$  ratio:

Zn  $L\beta_1$ : Zn 3d  $\rightarrow$  Zn 2p<sub>1/2</sub>  
*indicative for Zn-Zn bonds*

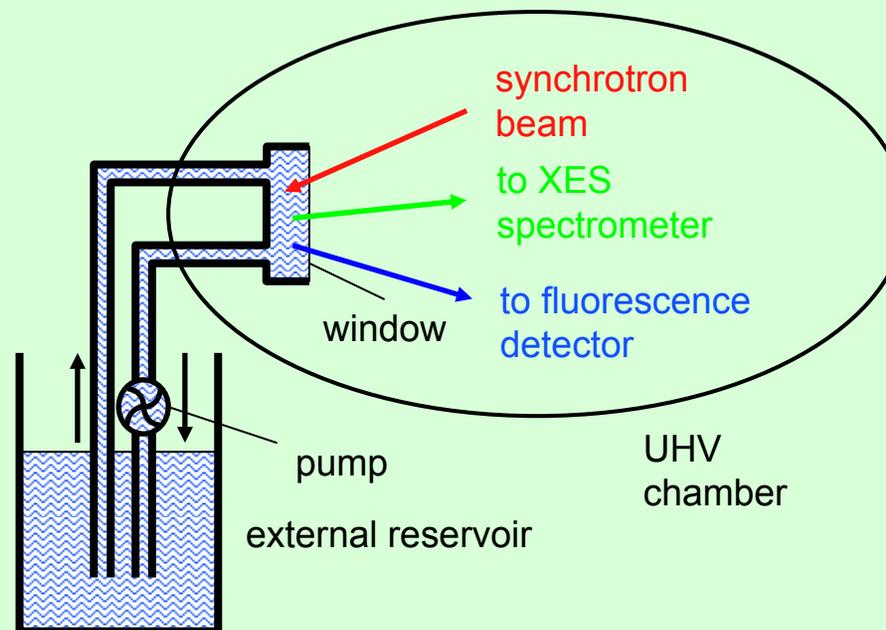
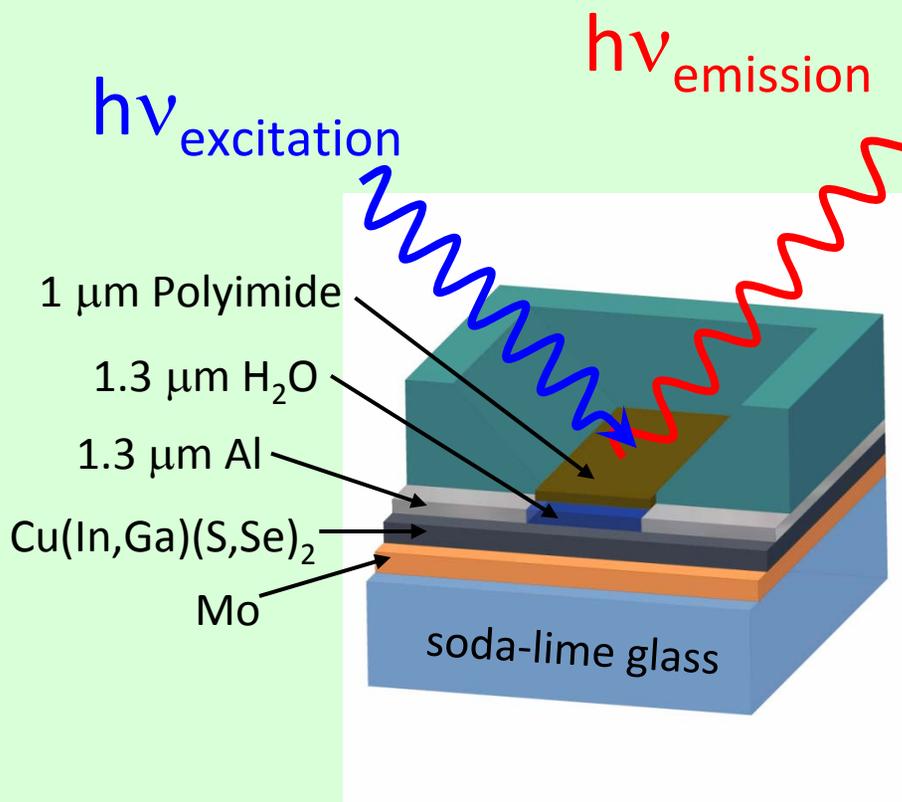
Zn 3d  $\rightarrow$  O 1s  
*indicative for Zn-O bonds*

assuming that the investigated layers are composed of ZnO and  $Zn_3N_2$ , the  $Zn_3N_2/(ZnO+Zn_3N_2)$  ratio can be estimated.

➤ **Key tool in understand of bulk properties**

## Key Future Direction: *In-situ* Soft X-ray Spectroscopy

- Understanding the impact of the Helmholtz layer
- Monitoring stability under illumination
- Deriving chemical and electronic information as a function of environmental parameters



➤ **Key in-situ tool needed to understand real PEC interface behavior**

J. Chem. Phys. **119**, 10467 (2003)  
 Appl. Phys. A **78**, 829 (2004)  
 Nucl. Instrum. Methods A **585**, 172 (2008)

# Specific Focus Materials *DOE-SHGR PEC*

*PEC "Tool-Chest" Employed by SHGR Team in R&D of:*

*work in this presentation*

- **Tungsten-Based Compound Films (UH, Intematix)**
  - Modified Tungsten Oxide Compounds with Anion/Cation Substitutions
- **Copper Chalcopyrite Compound Films (UH)**
  - Copper-Indium-Gallium-Selenium-Sulfur Compounds
- **Silicon-Based Compound Films (MVSystems, UH)**
  - Amorphous Silicon Carbide Films with p- and n- type Doping
- **Iron-Based Compound Films (UCSB)**
  - Novel Iron-Based Compound Materials, including Fe<sub>2</sub>O<sub>3</sub> Nanorods
- **Zinc-Based Compound Films (NREL)**
  - Modified Zinc Oxide Compounds with Anion/Cation Substitution



# Tungsten-Based Material *DOE-SHGR PEC*

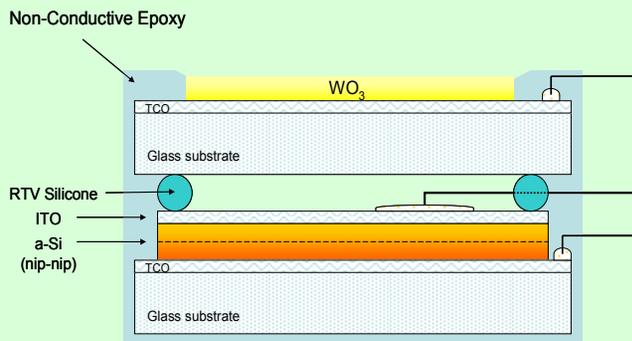
*Tungsten oxide is a model material to study PEC hydrogen generation...*

## *promise*

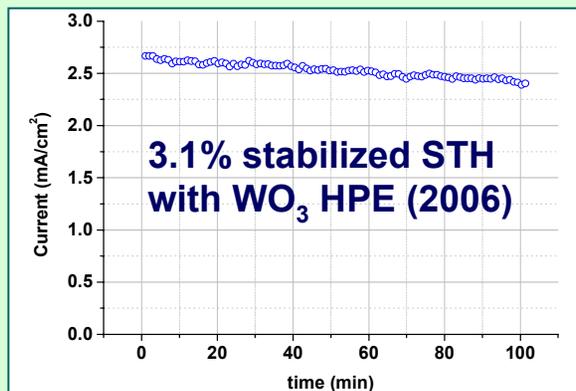
- Sufficient absorption to generate moderate photocurrents (2.6eV)
- Good electron transport properties
- High Stability in Electrolytes
- Thin film process scalable
- Demonstrated in prototype multi-junction devices

## *challenge*

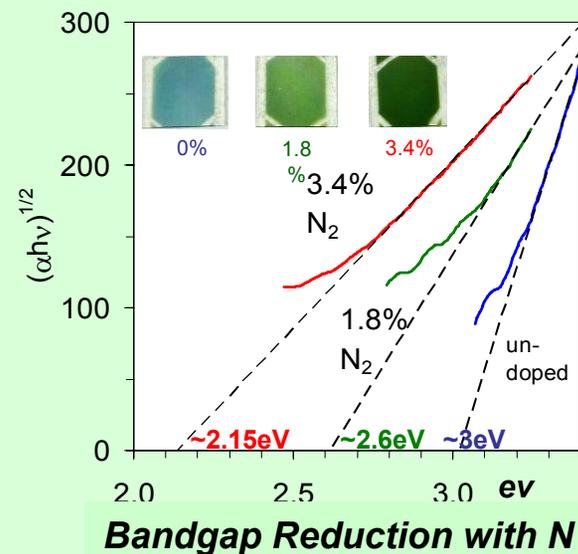
- Non ideal band edge alignment – requires supplemental bias
- Bandgap requires reduction to increase photocurrents
- The photo-stability over extended time periods and for new tungsten-alloy compositions requires validation



**Mechanically-Stacked  
HPE Device Configuration**



**H<sub>2</sub>-Production Photocurrent**



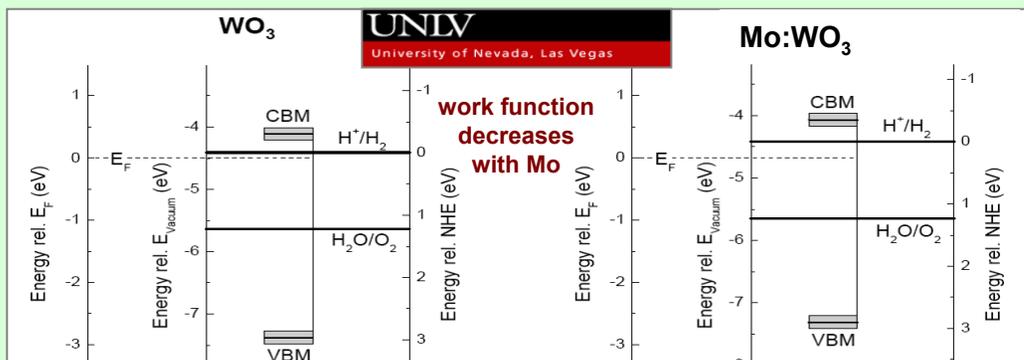
**Bandgap Reduction with N**

## key previous project results

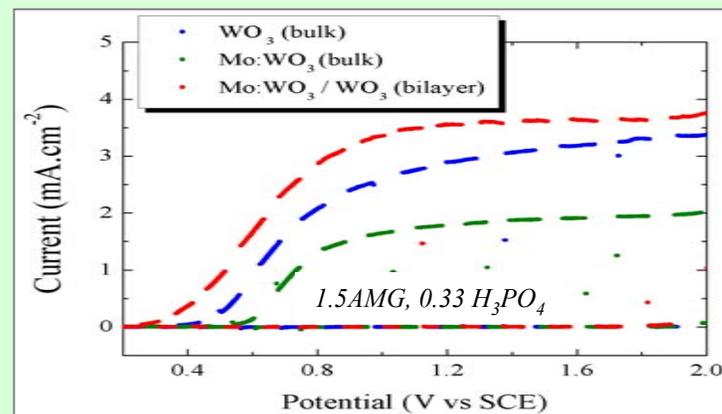
- High-quality WO<sub>3</sub> films developed with AM1.5 PEC photocurrents of 3.0 mA/cm<sup>2</sup> (synthesized using low-temperature process)
- Nitrogen incorporation in WO<sub>3</sub> films reduced optical bandgap from 2.6eV to 2.1eV; **BUT** disrupted grain structure & transport properties, reducing PEC photocurrents

## key recent project results

- Molybdenum incorporation in the bulk WO<sub>3</sub> films resulted in moderate increase in absorption, **BUT** also disrupts grain structure
- Molybdenum incorporation at the surface improves interface properties, yielding new-benchmark AM1.5 PEC photocurrents of 3.5 mA/cm<sup>2</sup>



Band diagrams obtain from UPS and IPES analyses, Marcus Baer

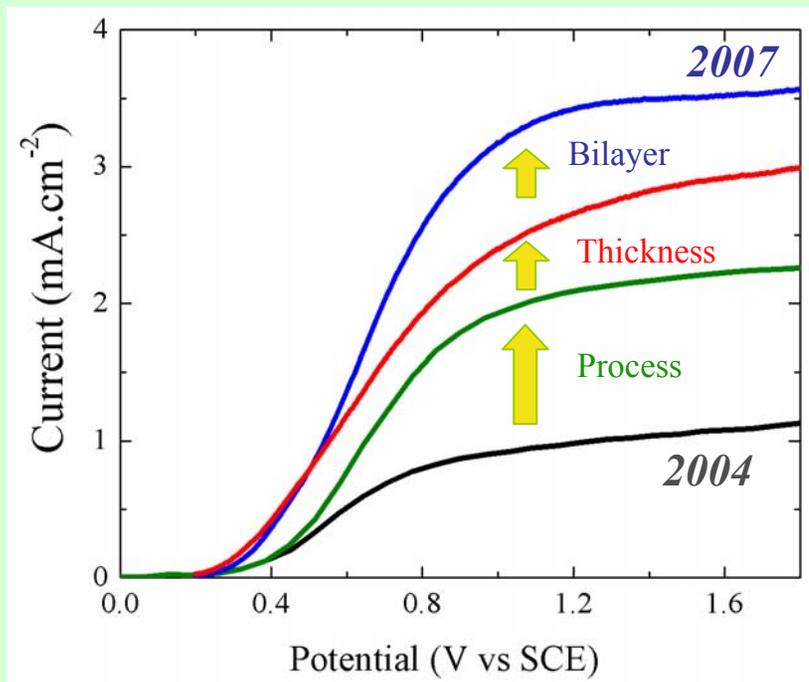


Mo/WO<sub>3</sub> PEC photocurrents

# WO<sub>3</sub> Material Progress

DOE-SHGR PEC

↑ improvements in WO<sub>3</sub> PEC performance



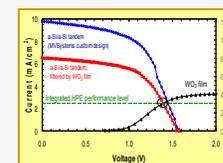
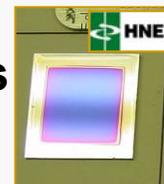
Year	Focus	saturated J <sub>photo</sub>
2004	Initial depositions	1.1 mA/cm <sup>2</sup>
2005	Process optimization (film stoichiometry...)	2.3 mA/cm <sup>2</sup>
2006	Optimum thickness determination	3.0 mA/cm <sup>2</sup>
2007	Surface band shift using bilayer	3.5 mA/cm <sup>2</sup>

- Continued improvement in low-temp WO<sub>3</sub> film photocurrents and fill-factor (with considerable guidance from the ever improving PEC Tool-Chest)
- **STH efficiencies of 3.1%** (AM1.5) demonstrated HPE devices using 2006 films
- **STH efficiencies of 4%** (AM1.5) expected in HPE devices using 2007 films
- **100+ hours PEC stability** exhibited in optimized WO<sub>3</sub> films
- Further improvements contingent on reducing bandgap of the absorber material....

# *WO<sub>3</sub> Path Forward* **DOE-SHGR PEC**

## *Expand Collaborative Research Efforts to:*

- **Eliminate lattice defects for WO<sub>3</sub> with nitrogen incorporation**
  - New co-incorporation schemes (lessons learned from ZnO work)
  - New synthesis approaches
- **Pursue bandgap reduction using different anion / cation species**
  - Ternary and quaternary compounds suggested by theoretical work
- **Continue optimization of surface and interface**
  - Catalyst treatments and bi-layers
- **Continue demonstration of integrated multi-junction devices**
  - Analysis and design of PV/PEC Hybrid Photoelectrode device structures
  - Design of process-compatible fabrication sequence
  - Break the 5% STH barrier for 2.6eV WO<sub>3</sub>



*Continued Funding Secured through DOE-MVSystems Project*

# Amorphous SiC Material *DOE-SHGR PEC*

*Amorphous silicon carbide is a photoactive material with tunable bandgap, which would enable the fabrication of “all-silicon” multi-junction water-splitting devices*

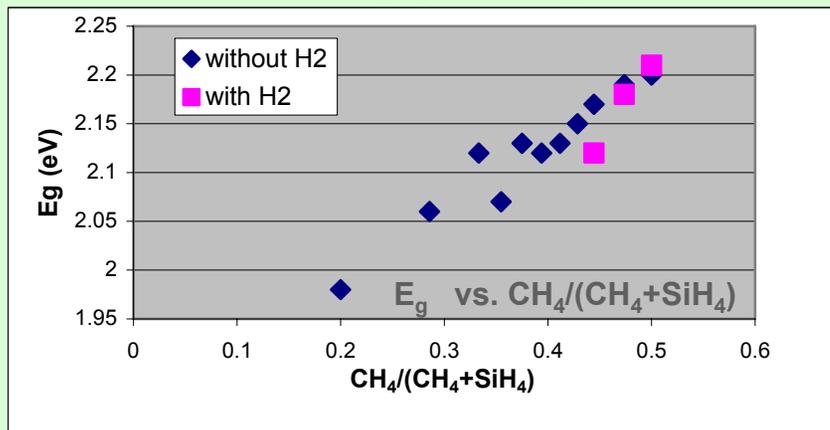
## promise

- Tunable bandgap of 2.0-2.3 eV and good optoelectronic quality
- Large knowledge-base from a-Si PV technology
- Enables “all-silicon multi-junction device” to be fabricated in a “cluster tool” machine

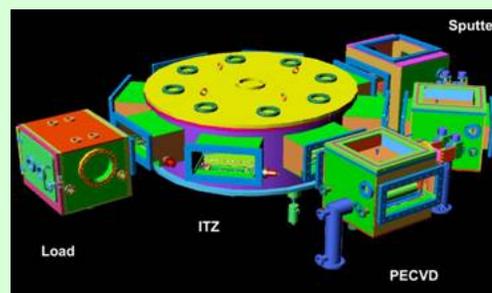
## challenge

- Non-ideal band edge alignment – requires supplemental bias
- Kinetic limitations apparent for bare a-SiC electrodes
- Long term corrosion and photo-corrosion behavior is not known

## Bandgap tuning



## Cluster-tool fabrication equipment



large-scale cluster tool design



reel-to-reel cassette\*

\* US patent #6,258,408B1: [MVSsystems](#)

# a-SiC Material Progress *DOE-SHGR PEC*

## key previous project results

- Process conditions established for device-quality a-SiC:H material
- Demonstration of PEC junctions with AM1.5 PEC photocurrents of 9 mA/cm<sup>2</sup>

## key recent project results

- Demonstration of optimized a-SiC:H materials & devices with >5% PV efficiencies
- Implementation of experiments to enhance corrosion resistance
- Implementation of advanced bulk & surface characterizations to help find solutions to potential-offset and fill-factor limitations

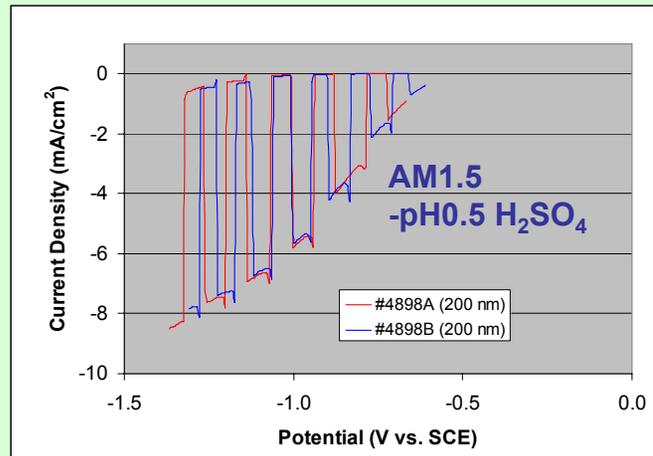
### test configuration

a-SiC(i) (200nm, 1.9~2.1eV)

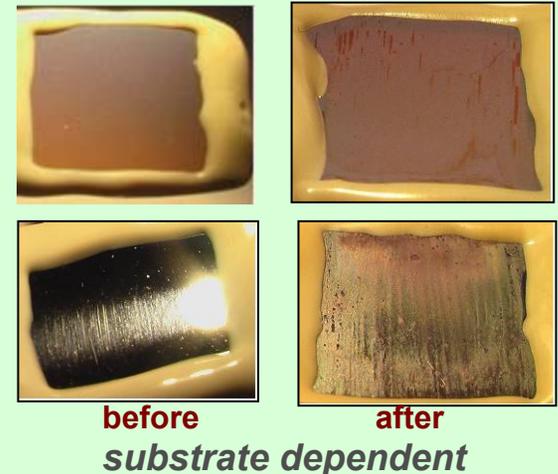
a-SiC(p) (20 nm)

Substrate (various types)

### PEC photocurrents



### corrosion work



## *Expand Collaborative Research Efforts to:*

- **Continue comprehensive PEC characterization of a-SiC photoelectrodes**
  - band positions, electrode kinetics
  - long-term stability
- **Continue optimization of a-SiC bulk films**
  - enhanced PEC photocurrent and fill-factor
- **Continue optimization of surface and interface**
  - reduce potential-shift
  - enhance stability
- **Fabricate & characterize monolithic a-SiC/a-Si multijunction devices**
  - analysis and design of PV/PEC HPE device structures
  - manufacture-scale processing



***Continued Funding Secured through DOE-MVSystems Project***

# Cu-Chalcopyrite Progress *DOE-SHGR PEC*

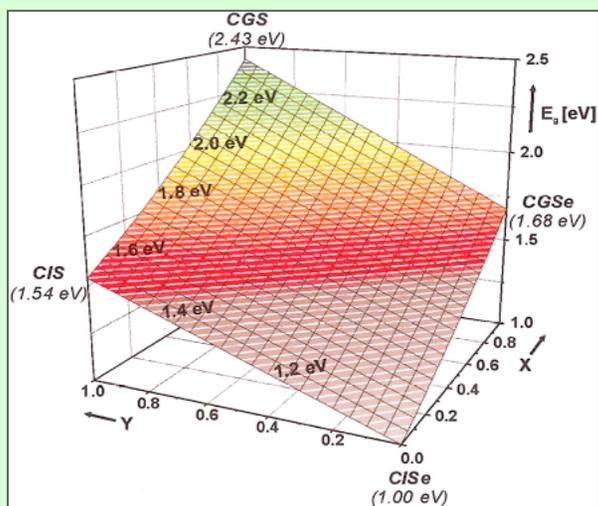
*Copper chalcopyrites are efficient absorber for thin-film solar cells and their optoelectronic properties are equally well-suited for photoelectrolysis*

## promise

- Direct bandgap and good carrier transport properties
- High PEC photocurrents demonstrated for p-type Cu(In,Ga)Se<sub>2</sub> electrodes
- Bandgap and band edges “tunable” by composition
- Synergy with PV CIGS multi-junction device research and development

## challenge

- Valence band edge of the Cu(In,Ga)Se<sub>2</sub> films too high
- Kinetic limitations apparent for bare electrodes
- Long term corrosion and photo-corrosion behavior is not known
- High-temperature fabrication steps



bandgap tuning in  $\text{Cu}(\text{In}_{(1-x)}\text{Ga}_x)(\text{S}_y\text{Se}_{(1-y)})_2$

$\text{CuInSe}_2$  ( $E_G=1.0$  eV)

$\text{CuIn}_{0.4}\text{Ga}_{0.6}\text{Se}_2$  ( $E_G=1.4$  eV)

$\text{CuGaSe}_2$  ( $E_G=1.68$  eV)

$\text{CuGaS}_2$  ( $E_G=2.43$  eV)

bandgap



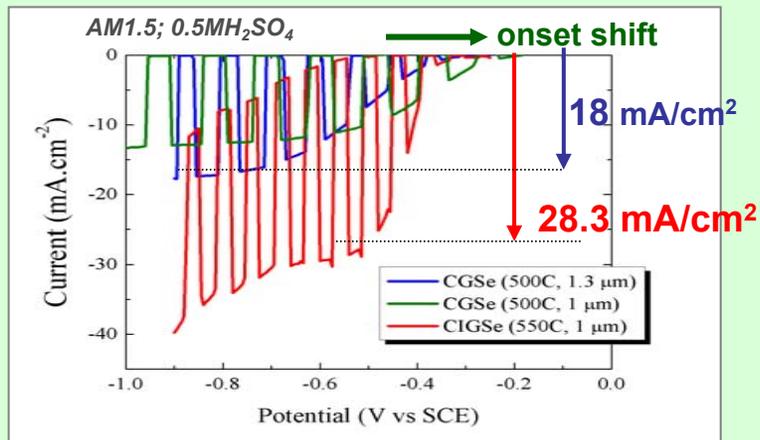
# Cu-Chalcopyrite Progress DOE-SHGR PEC

## key previous project results

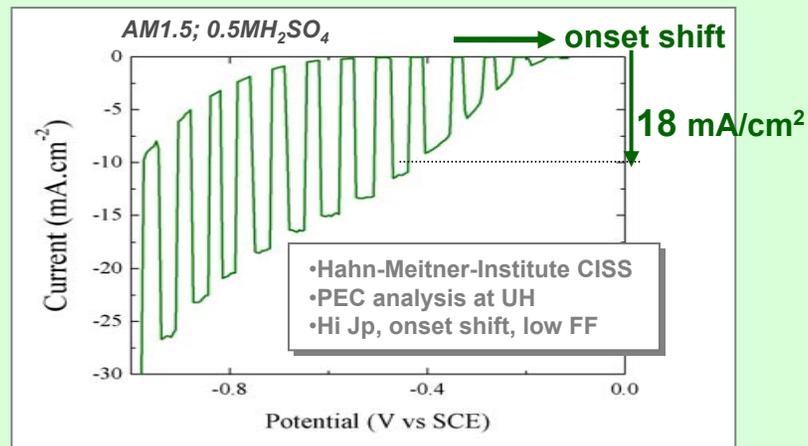
- PV-quality CIGSe films developed with AM1.5 PEC photocurrents of 28 mA/cm<sup>2</sup> (but with significant potential-shift needed due to flatband position)
- Demonstration of bandgap tuning using alloy variations

## key recent project results

- High-quality CGSe films developed with AM1.5 PEC photocurrents of 18 mA/cm<sup>2</sup> (potential-shift improved over CIGSe, but fill factor worse)
- Demonstration of H<sub>2</sub> photo-production at CGSe surface stable for >10 hours
- Initial investigation of sulfur incorporation for further favorable band-edge shifts



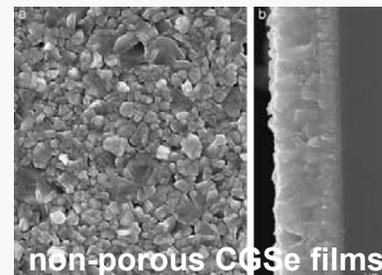
CIGSe & CGSe PEC electrodes



CuInS<sub>2</sub> PEC electrodes

## Expand Collaborative Research Efforts to:

- Continue comprehensive PEC characterization of Cu chalcopyrites
  - characterize bulk and surface band positions, transitions and states
  - in-situ PEC interface characterizations
- Develop device-quality materials with wider bandgap & lower valence band
  - fine-tune  $\text{Cu}(\text{In}_{(1-x)}\text{Ga}_x)(\text{S}_y\text{Se}_{(1-y)})_2$  alloy- including sulfur
  - graded  $\text{CuGaSe}_2$  (e.g., Cu-poor surfaces)
- Continue optimization of surface and interface
  - reduce potential-shift, and enhance kinetics and stability
- Develop stacking process for multi-junction device configurations



*Continued Funding Secured through DOE-MVSystems Project*

# PROGRAM SUMMARY *DOE-SHGR PEC*

## ➤ Collaborative Approach has been a Complete Success!

The SHGR team, working closely with the DOE PEC Working Group, has developed an impressive “Tool Chest” of theoretical, synthesis and characterization techniques and successfully applied it in the R&D of important focus PEC materials systems

## ➤ Major Technical Targets Met in Focus Materials Research:

### – Photocurrent target ( $>1.6\text{mA/cm}^2$ ) met in several films:

- *3.5 mA/cm<sup>2</sup> demonstrated in low temperature WO<sub>3</sub> films*
- *>9.0 mA/cm<sup>2</sup> demonstrated in amorphous silicon carbide*
- *>18 mA/cm<sup>2</sup> demonstrated in copper chalcopyrite films*

### – Conversion efficiency target (2-8% STH) met in HPE devices:

- *3.1% STH efficiency demonstrated using 2006 WO<sub>3</sub>*
- *4% STH efficiency expected using recent bi-layer WO<sub>3</sub>*

### – Stability target (100 hour durability) met:

- *>100 hour stable operation demonstrated using WO<sub>3</sub>*

## ➤ Funding Avenues Secured for the Follow-On Research Needed to Reach the Long-Term DOE Hydrogen Production Goals

# FUTURE WORK *DOE-SHGR PEC*

- **Continue Current PEC R&D and Optimization Efforts Under New Funding Umbrellas **MVSystems****
  - Focus material R&D: tungsten-, silicon-, chalcopyrite-, iron-based compounds
  - Accelerate interface, device and system development work
  
- **Continue DOE PEC Working Group Efforts**
  - Further PEC “Tool-Chest” development efforts
  - Standardization of materials and device testing protocols
  - Refinement of materials selection and prioritization criteria
  
- **Expansion of Collaboration Efforts: Nationally and Internationally**
  - DOE PEC Working Group Expansion
  - USA-led “International Energy Agency PEC Annex-26” offshoot of SHGR work
  - “International Partnership for a Hydrogen Economy” program proposal
  
- **Materials & Device Breakthroughs for High-Efficiency, Low-Cost PEC Hydrogen Production!**