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

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

OVERVIEW

PEC WORKING GROUP

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*
- ➢ *MVSystems 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

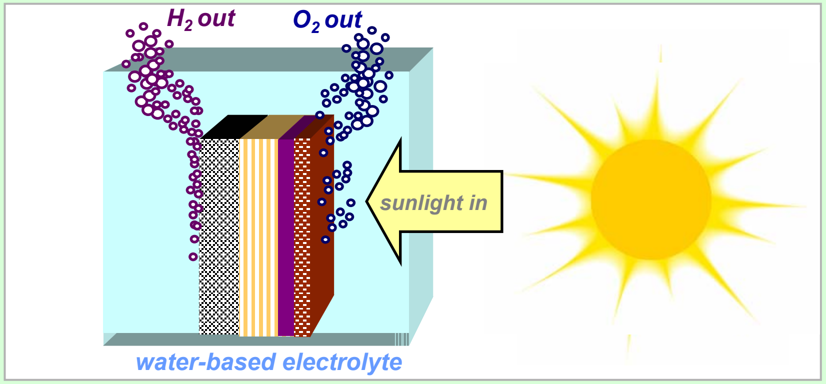
DOE PEC Program Targets

Table 3.1.10. Technical Targets: Photoelectrochemical Hydrogen Production[a]

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

photoelectrode-based PEC solar-H_2 production:

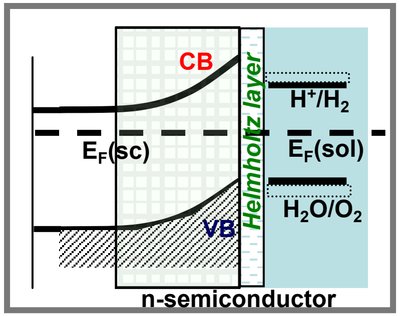
must out-perform PV/electrolysis



THE PEC CHALLENGE

NO **Material System satisfies *ALL* requirements to efficiently split H_2O…**
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

APPROACH PEC WORKING GROUP

- ***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 Spinels, 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

UNLV UNIVERSITY OF NEVADA LAS VEGAS | HNEI | NREL | UCSB | Intematix | MVSystems | Altairnano innovation at work

SHGR PEC subtask collaborators

OVERVIEW DOE-SHGR PEC

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_2 production devices:

  → Target Range: 1.6 – 6.5 mA/cm^2 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

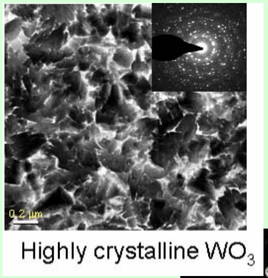
- Explore avenues toward manufacture-scaled devices and systems

APPROACH DOE-SHGR PEC

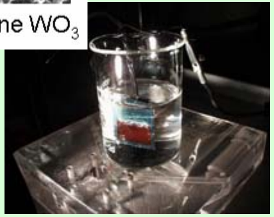
➤*Develop & Refine the PEC "TOOL-CHEST":*

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

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



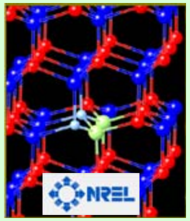
Highly crystalline WO_3

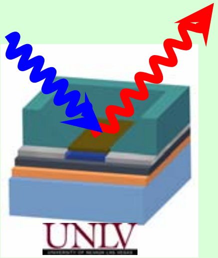


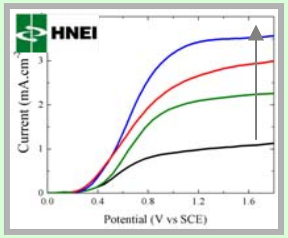
- **TUNGSTEN -Based Compounds**
- **SILICON-Based Compounds**
- **COPPER-CHALCOPYRITE Compounds**
- **ZINC-OXIDE -Based Compounds**
- **IRON-OXIDE -Based Compounds**
- **Others (outside of SHGR umbrella)**

PROGRESS OVERVIEW

- ➢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







Theory Advances

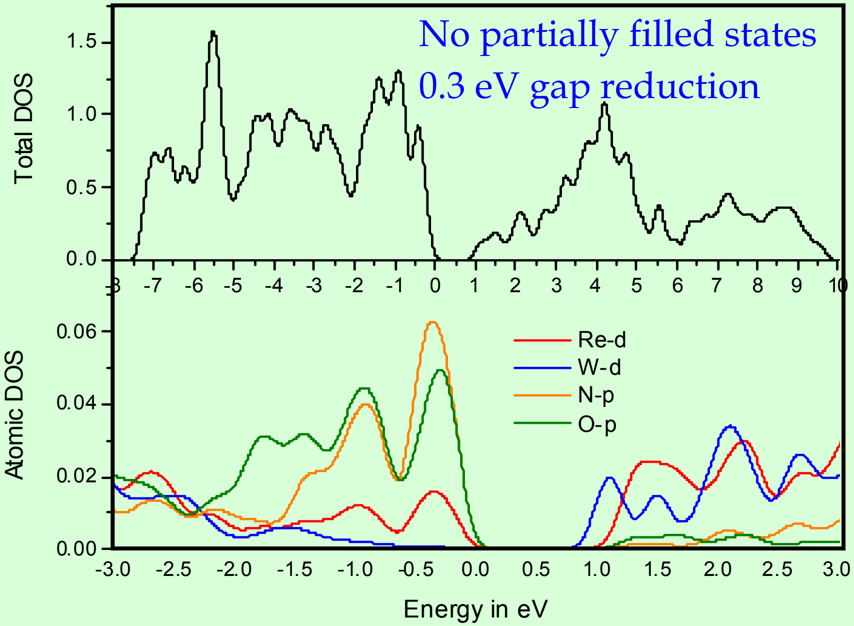
DOE-SHGR PEC

Density Functional theory study of metal-oxides: Band engineering for better PEC[*]

WO$_3$ Systems

theory provides invaluable guidance in tungsten-based materials

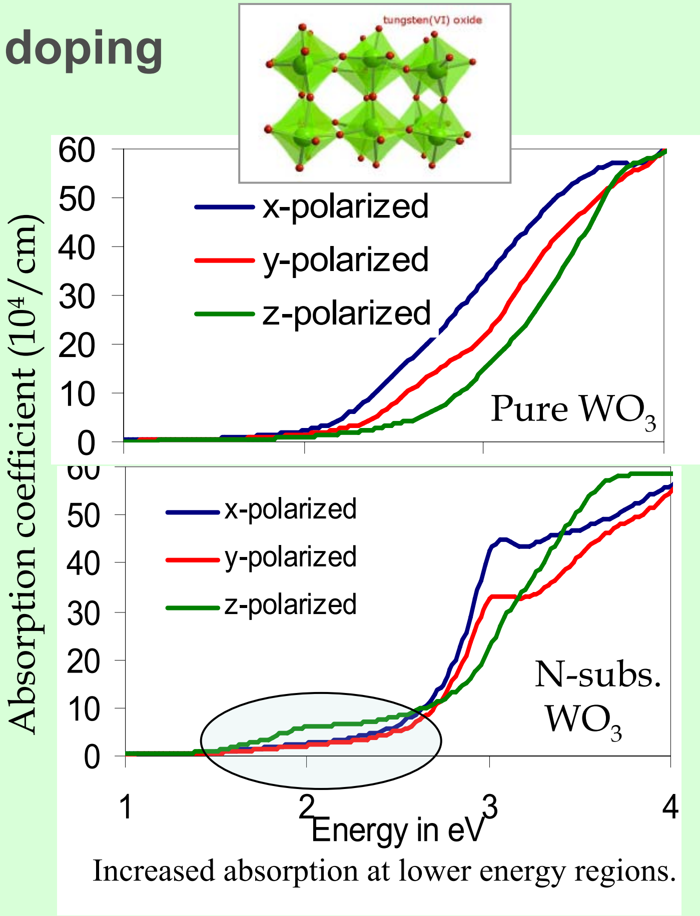
- Band gap and positions can be modified by doping
- Co-incorporation can enhance performance



No partially filled states

0.3 eV gap reduction

Re-N co-doping reduces recombination



Increased absorption at lower energy regions.

*M.N. Huda, A. Walsh, Yanfa Yan, S.-H. Wei, M. Al-Jassim, and J. Turner: National Renewable Energy Laboratory

Theory Advances

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

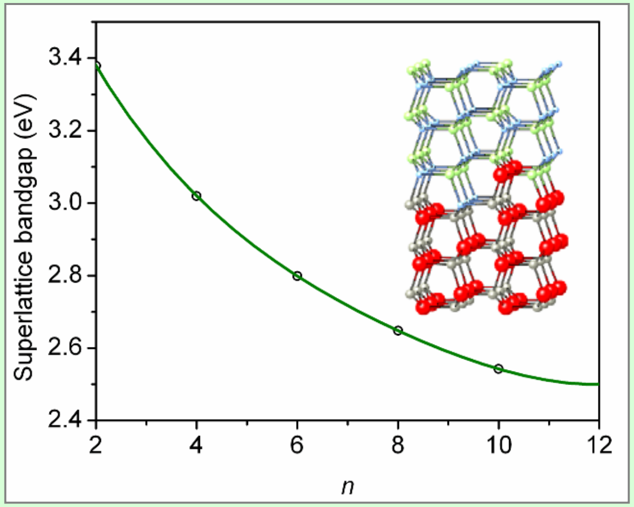
ZnO:GaN Systems

theory provides general guidance in synthesis of mixed-metal oxides

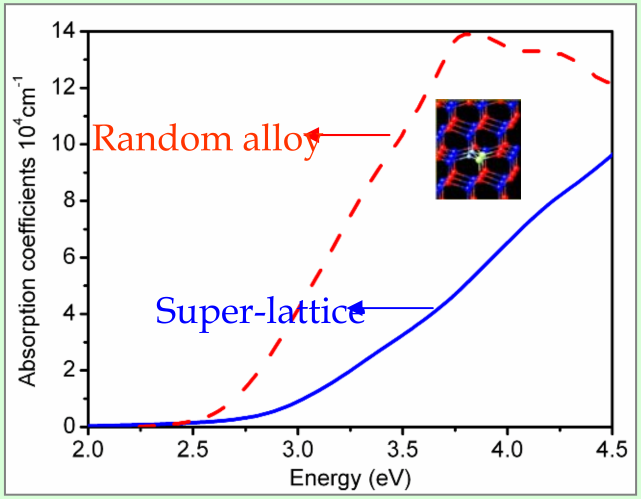
- **ZnO-GaN results in reduced band gap**
- **Band gap reduction is asymmetric**
- **ZnO is a better host than GaN**
- **Random alloy system is more effective than the super-lattice system**

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

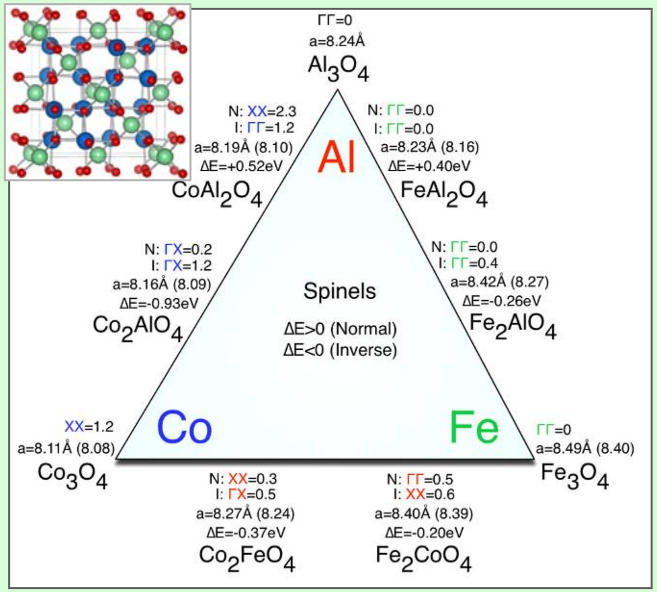
Theory Advances

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

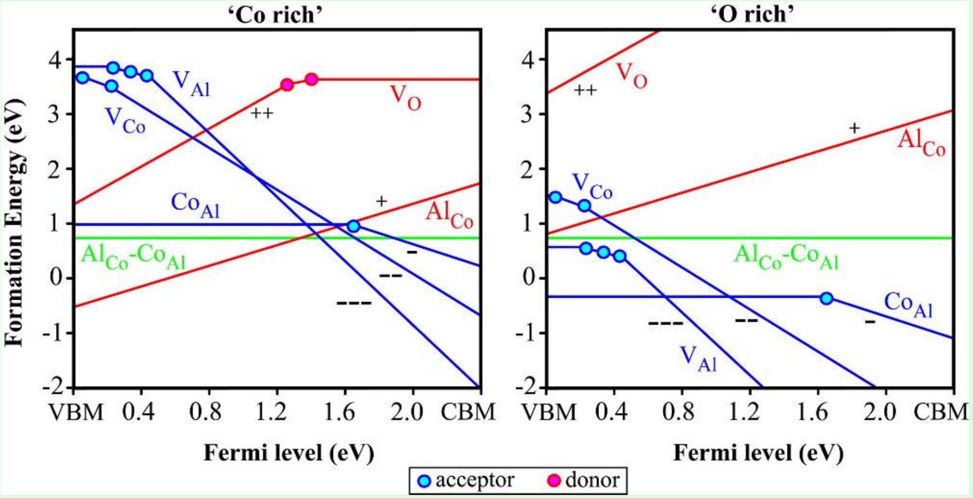
Co-Fe-Al Spinel Systems

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 $CoAl_2O_4$ 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.

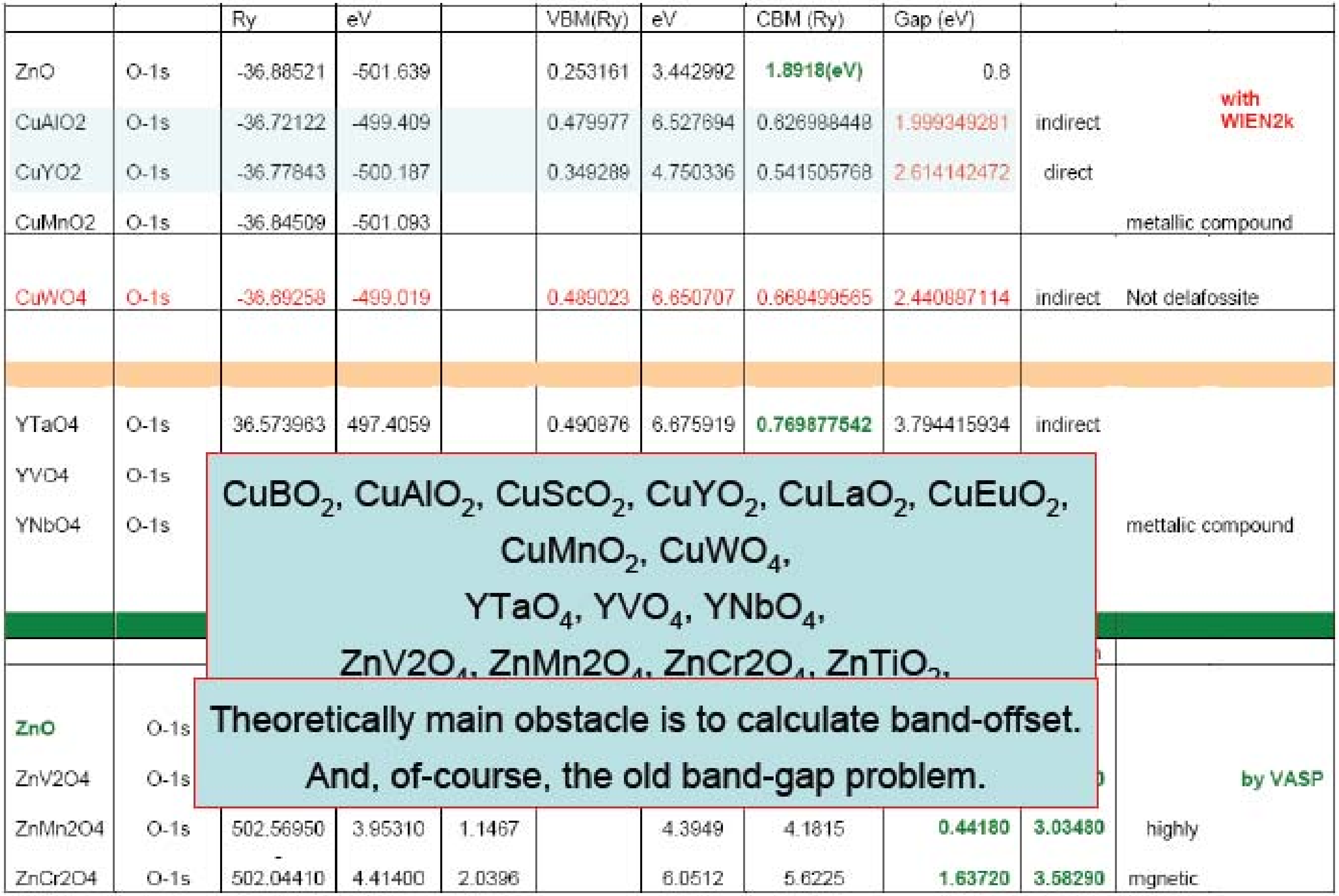


(Left) Calculated intrinsic defect formation energies as a function of the Fermi level under Co rich and O rich conditions

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	1.8918(eV)	0.8		
CuAlO2	O-1s	-36.72122	-499.409		0.479977	6.527694	0.626988448	1.999349281	indirect	with WIEN2k
CuYO2	O-1s	-36.77843	-500.187		0.349289	4.750336	0.541505768	2.614142472	direct	
CuMnO2	O-1s	-36.84509	-501.093							metallic compound
CuWO4	O-1s	-36.69258	-499.019		0.489023	6.650707	0.668499565	2.440887114	indirect	Not delafossite
YTaO4	O-1s	36.573963	497.4059		0.490876	6.675919	0.769877542	3.794415934	indirect	
YVO4	O-1s									
YNbO4	O-1s									mettalic compound
ZnO	O-1s									
ZnV2O4	O-1s									by VASP
ZnMn2O4	O-1s	502.56950	3.95310	1.1467		4.3949	4.1815	0.44180	3.03480	highly
ZnCr2O4	O-1s	- 502.04410	4.41400	2.0396		6.0512	5.6225	1.63720	3.58290	mgnetic

CuBO$_2$, CuAlO$_2$, CuScO$_2$, CuYO$_2$, CuLaO$_2$, CuEuO$_2$,
CuMnO$_2$, CuWO$_4$,
YTaO$_4$, YVO$_4$, YNbO$_4$,
ZnV2O$_4$, ZnMn2O$_4$, ZnCr2O$_4$, ZnTiO$_2$,

Theoretically main obstacle is to calculate band-offset.
And, of-course, the old band-gap problem.

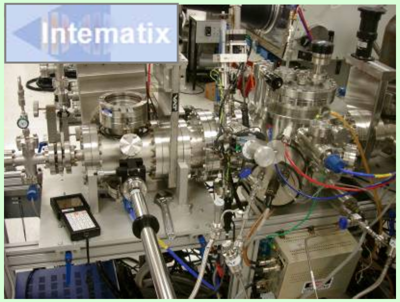
Diverse Synthesis Routes

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

Co-Evaporation system for copper chalcopyrite films



Automated combinatorial physical-vapor-deposition system

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

Characterization Progress

- ***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)

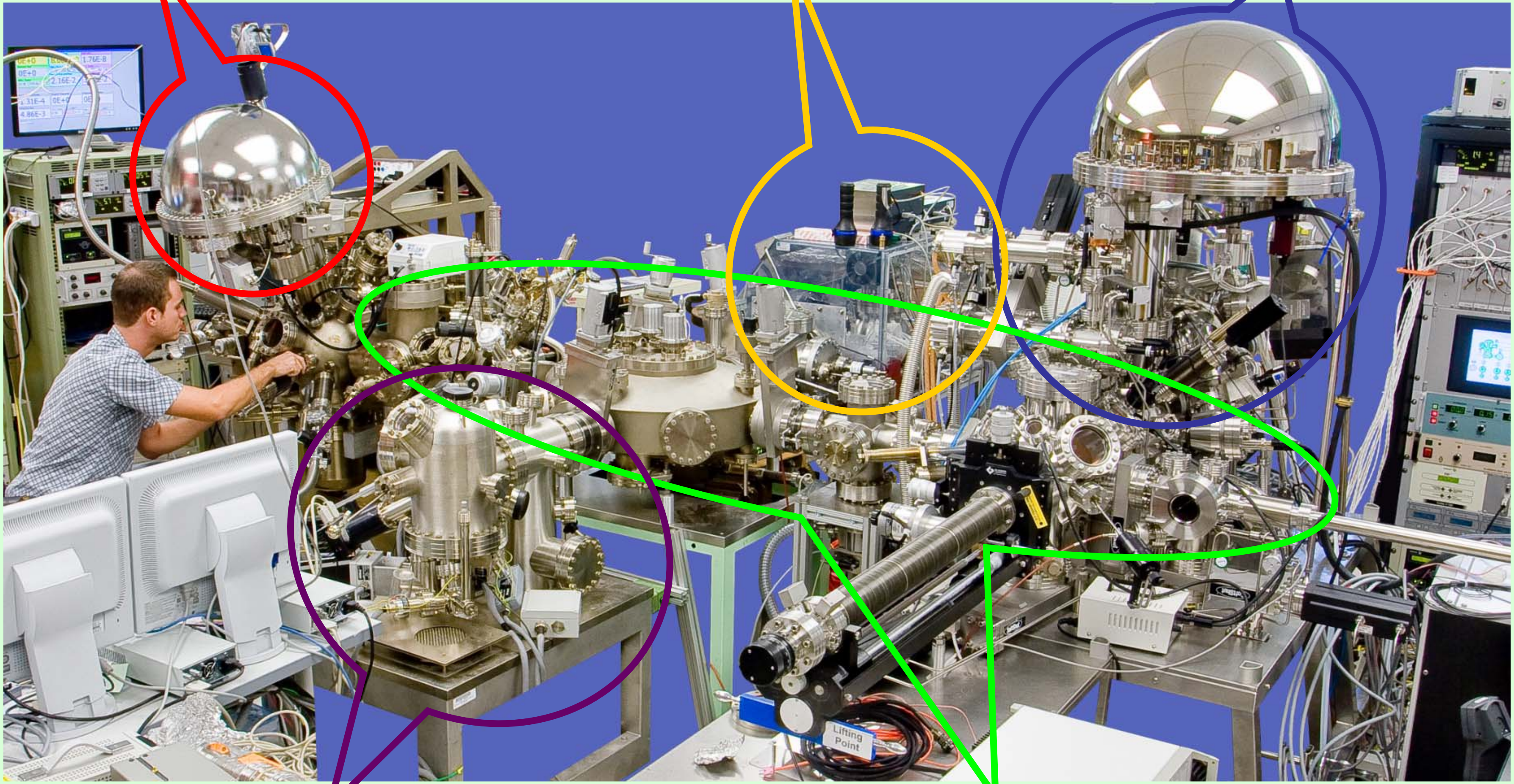
Characterization Progress

DOE-SHGR PEC

High dynamic range
XPS, UPS, Auger, IPES

Glovebox

High resolution
XPS, UPS, Auger



Scanning Probe
Microscope

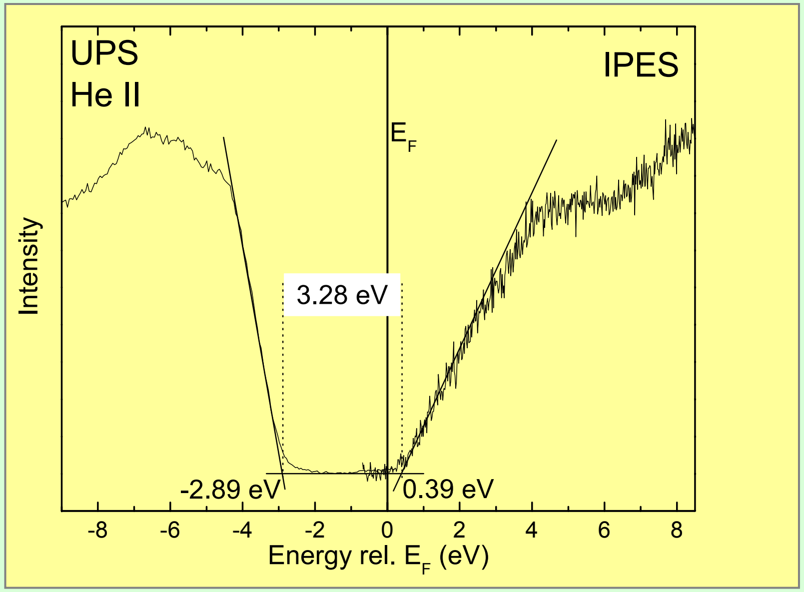
UNLV
UNIVERSITY OF NEVADA LAS VEGAS

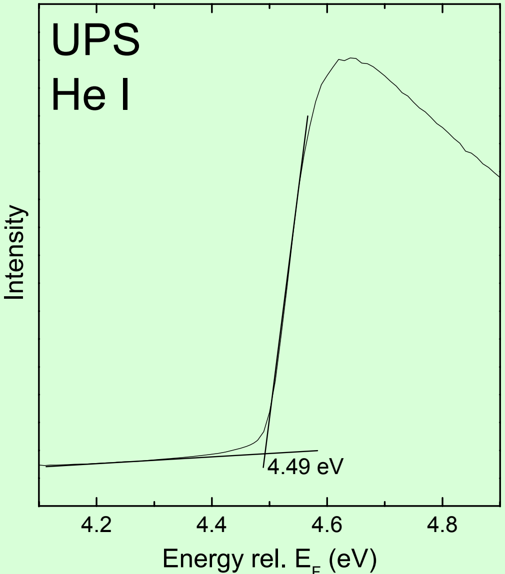
Sample preparation and
distribution

Characterization Progress

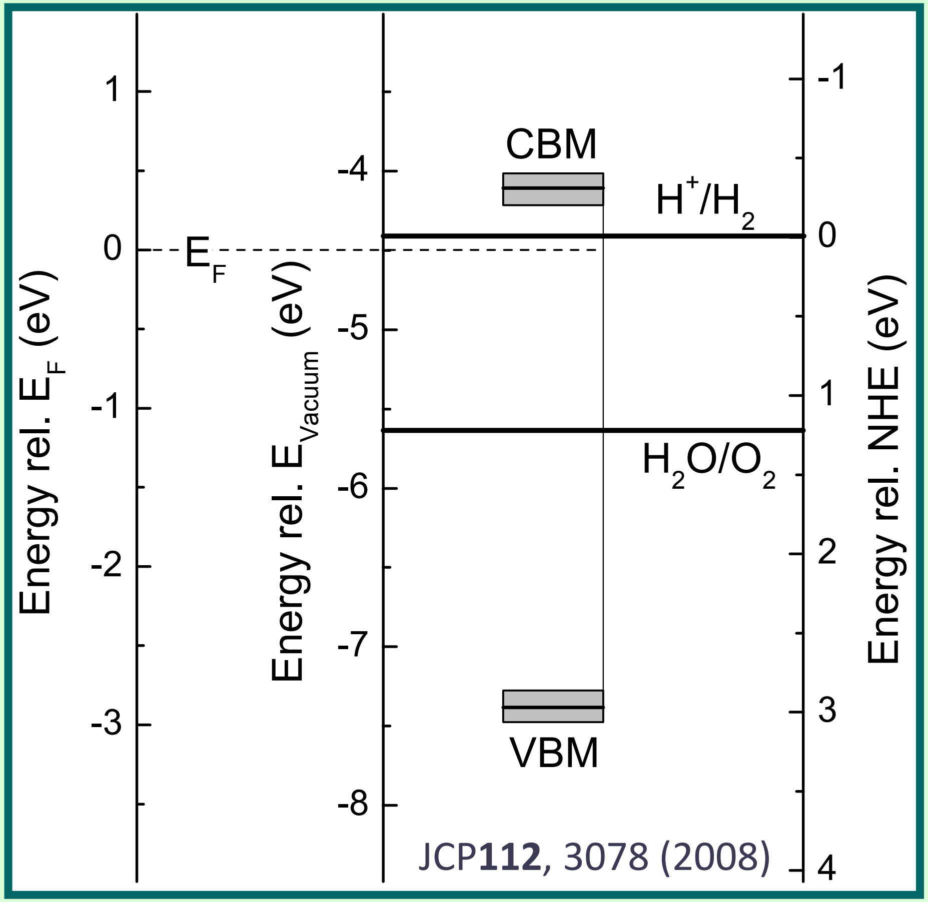
DOE-SHGR PEC

First all-experimental depiction of the WO_3 surface electronic structure





Combining direct and inverse photoelectron spectroscopy



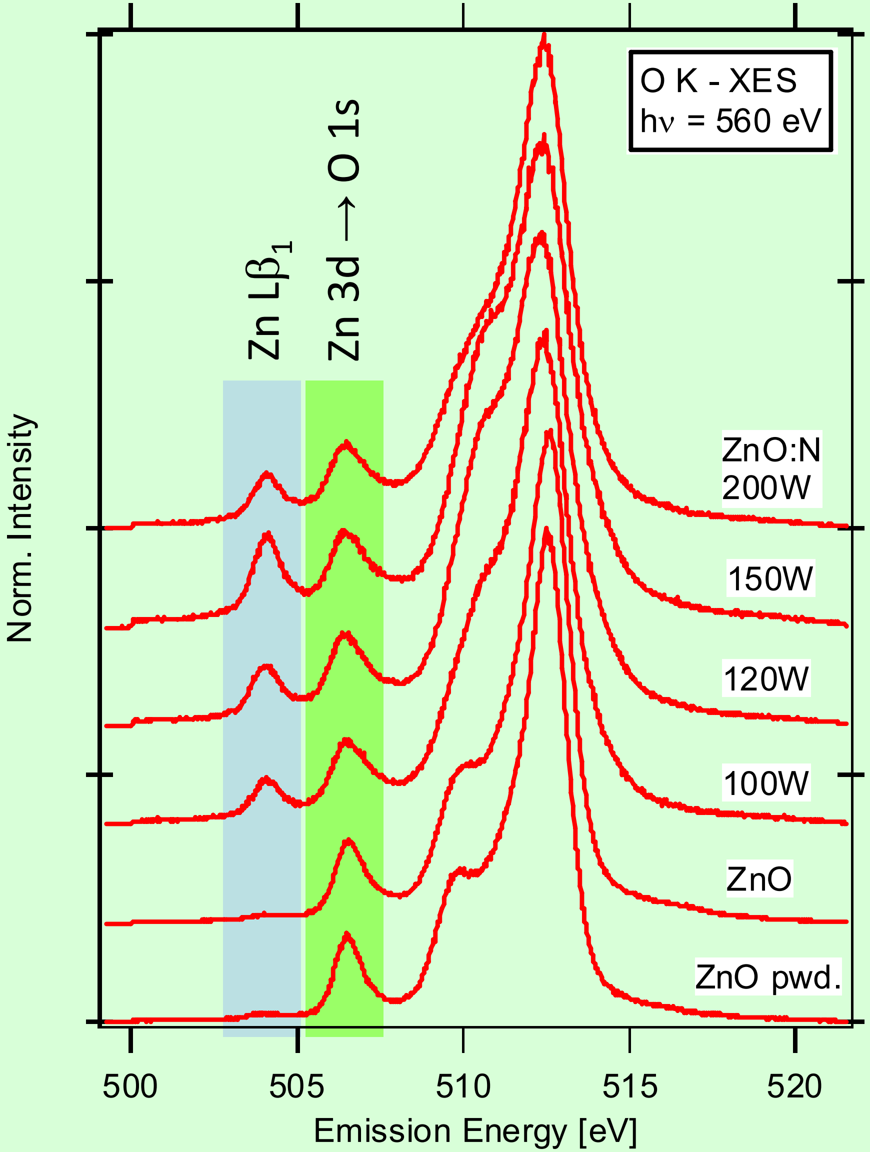
JCP**112**, 3078 (2008)

- ➢ **Invaluable asset in understand of material surface electronic states**

Characterization Progress

DOE-SHGR PEC

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 Lβ$_1$: Zn 3d → Zn 2p$_{1/2}$
indicative for Zn-Zn bonds

Zn 3d → O 1s
indicative for Zn-O bonds

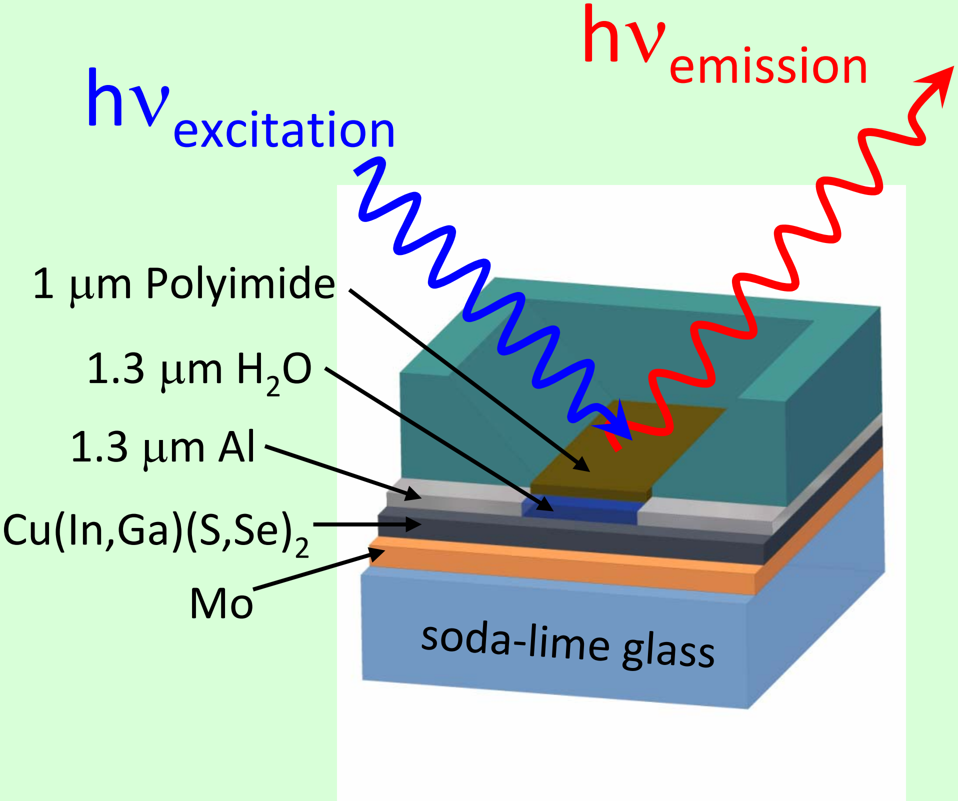
assuming that the investigated layers are composed of ZnO and Zn_3N_2, the *Zn_3N_2/ $(ZnO+Zn_3N_2)$ ratio* can be estimated.

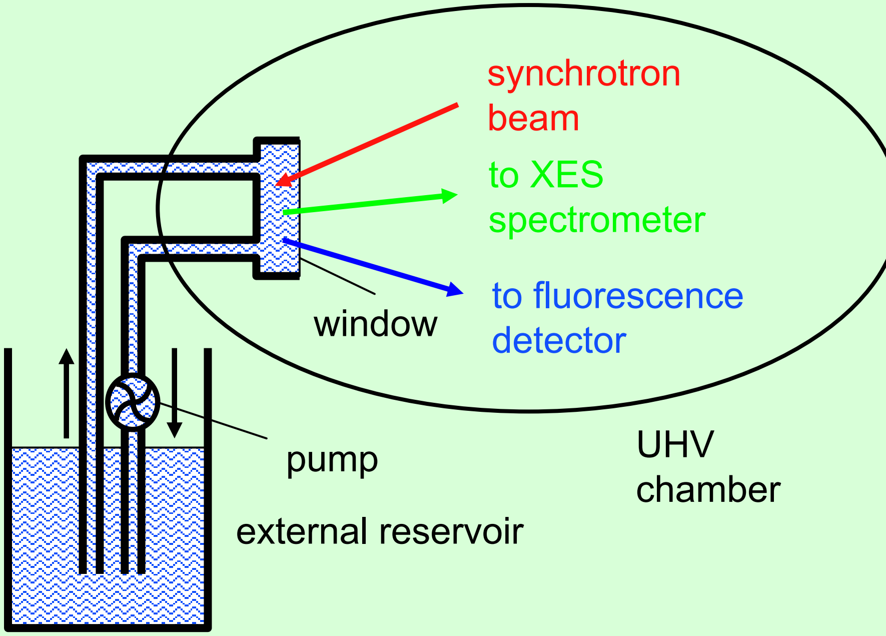
- **Key tool in understand of bulk properties**

Characterization Progress

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_2O_3 Nanorods
- **Zinc-Based Compound Films (NREL)**
  - –Modified Zinc Oxide Compounds with Anion/Cation Substitution

HNEI UNLV UNIVERSITY OF NEVADA LAS VEGAS NREL UCSB Intematix MVSystems Altairnano innovation at work

Tungsten-Based Material

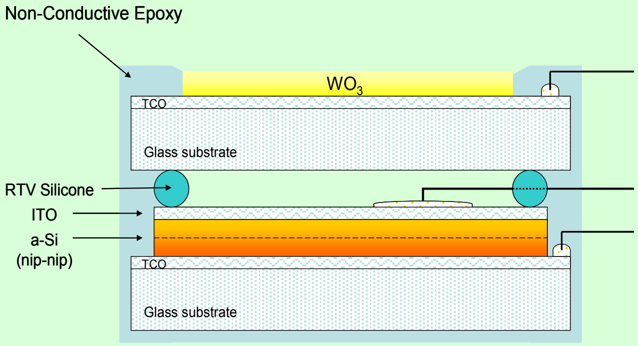
Tungsten oxide is a model material to study PEC hydrogen generation…

promise

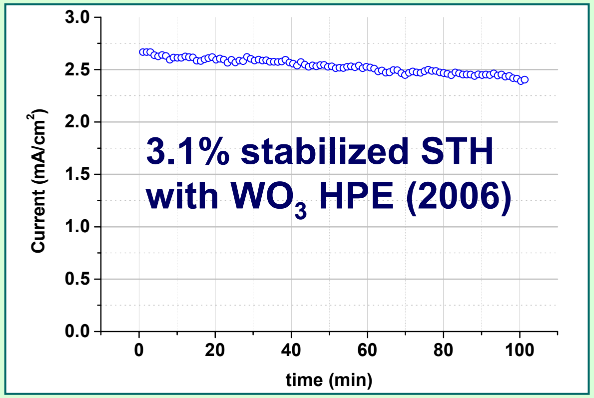
- **Sufficient absorption to generate moderate photocurrents (2.6eV)**
- **Good electron transport properties**
- **High Stability in Electrolytes**
- **Thin film process scalable**
- **Demonstrated in prototype multi-junction devices**

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**

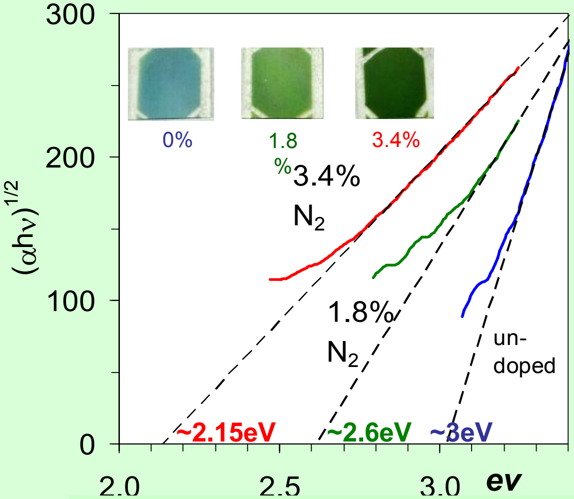


Mechanically-Stacked HPE Device Configuration



3.1% stabilized STH with WO_3 HPE (2006)

H_2-Production Photocurrent



Bandgap Reduction with N

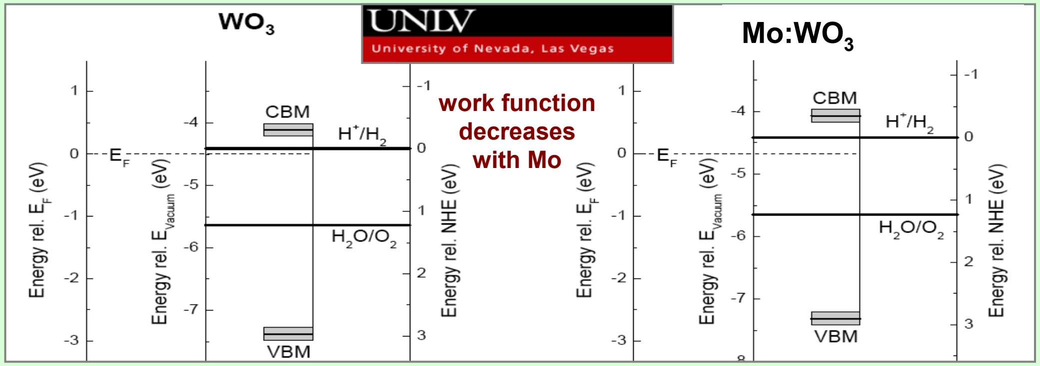
WO_3 Material Progress

key previous project results

- High-quality WO_3 films developed with AM1.5 PEC photocurrents of 3.0 mA/cm^2 (synthesized using low-temperature process)
- Nitrogen incorporation in WO_3 films reduced optical bandgap from 2.6eV to 2.1eV; *BUT* disrupted grain structure & transport properties, reducing PEC photocurrents

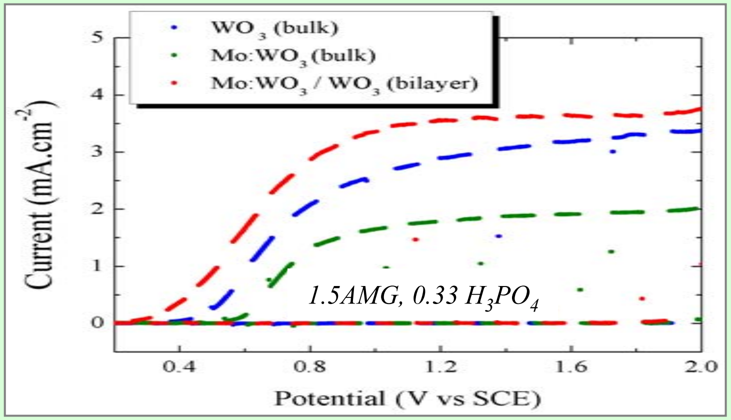
key recent project results

- Molybdenum incorporation in the bulk WO_3 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^2



Band diagrams obtain from UPS and IPES analyses, **Marcus Baer**

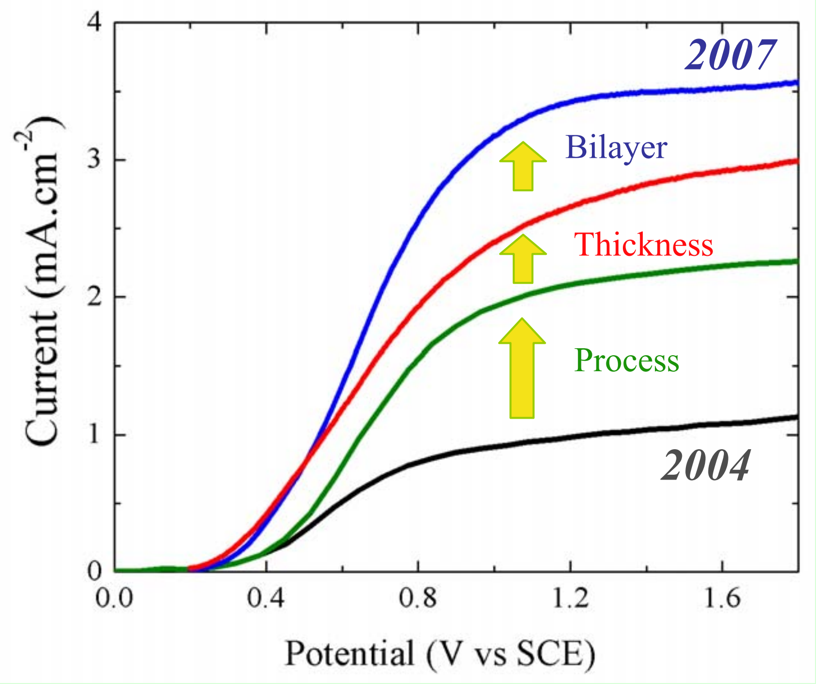
Weinhardt *et al.*, J. Phys. Chem. C, Vol. 112, No. 8, 2008



Mo/WO_3 PEC photocurrents

WO_3 Material Progress

↑ improvements in WO_3 PEC performance



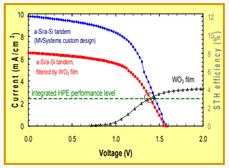
Year	Focus	saturated J_{photo}
2004	Initial depositions	1.1 mA/cm²
2005	Process optimization (film stoichiometry…)	2.3 mA/cm²
2006	Optimum thickness determination	3.0 mA/cm²
2007	Surface band shift using bilayer	3.5 mA/cm²

- **Continued improvement in low-temp WO_3 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_3 films**
- **Further improvements contingent on reducing bandgap of the absorber material….**

WO_3 Path Forward

Expand Collaborative Research Efforts to:

- Eliminate lattice defects for WO_3 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_3



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

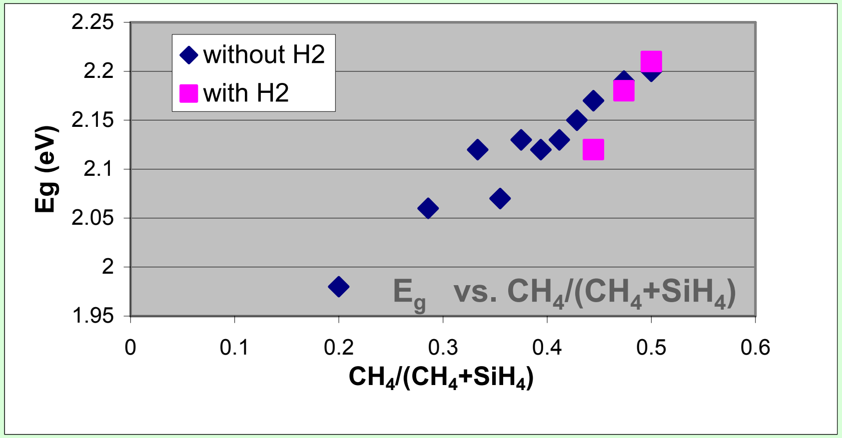
promise

- **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**

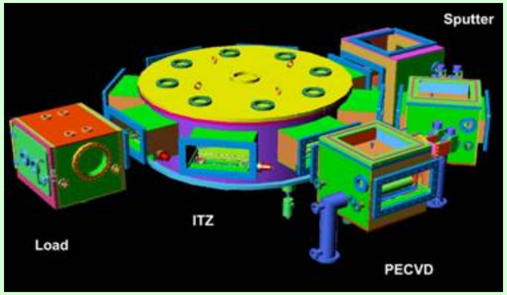
challenge

- **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: **MVSystems**

a-SiC Material Progress

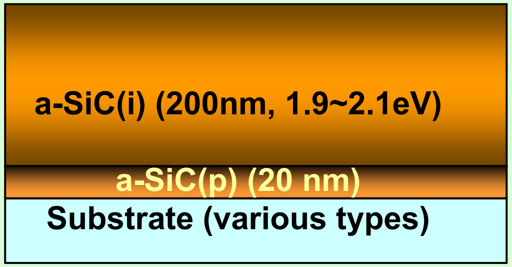
key previous project results

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

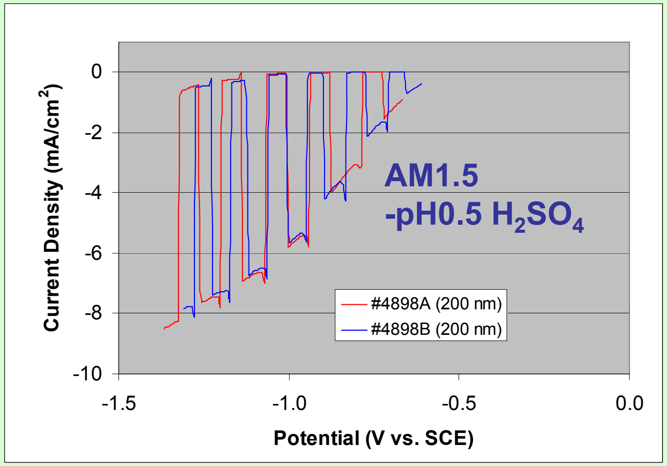
key recent project results

- 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

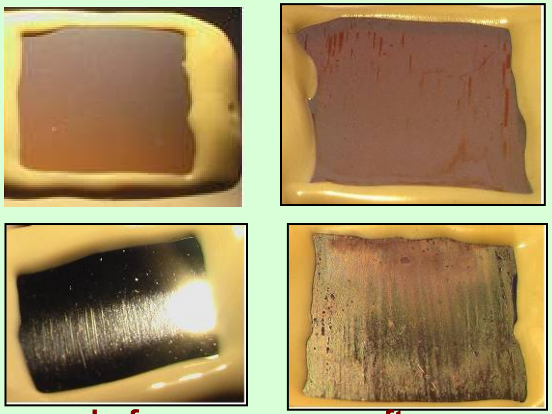
test configuration



PEC photocurrents



corrosion work



substrate dependent

a-SiC Path Forward

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

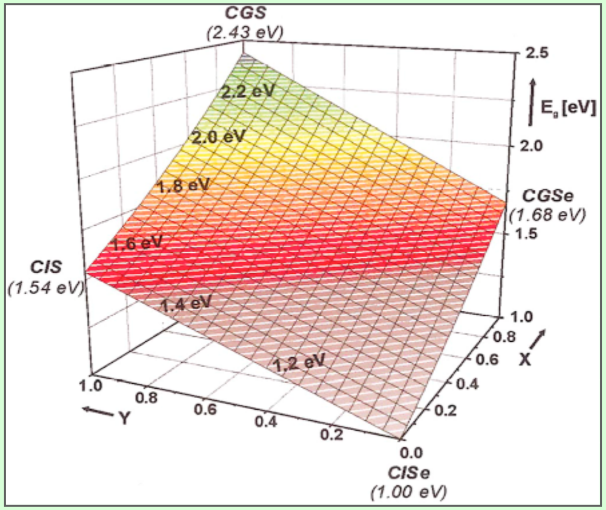
Copper chalcopyrites are efficient absorber for thin-film solar cells and their optoelectronic properties are equally well-suited for photoelectrolysis

promise

- **Direct bandgap and good carrier transport properties**
- **High PEC photocurrents demonstrated for p-type Cu(In,Ga)Se_2 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_2 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 $Cu(In_{(1-x)}Ga_x)(S_ySe_{(1-y)})_2$

$CuInSe_2$ (E_G=1.0 eV)
$CuIn_{0.4}Ga_{0.6}Se_2$ (E_G=1.4 eV)
$CuGaSe_2$ (E_G=1.68 eV)
$CuGaS_2$ (E_G=2.43 eV)

bandgap

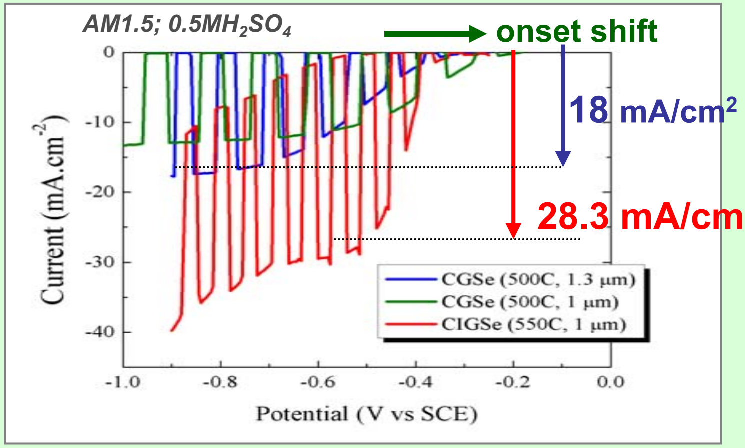
Cu-Chalcopyrite Progress

key previous project results

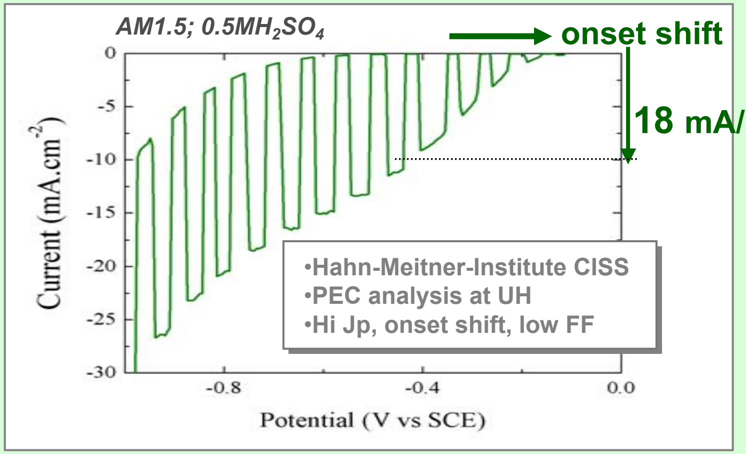
- **PV-quality CIGSe films developed with AM1.5 PEC photocurrents of 28 mA/cm^2** *(but with significant potential-shift needed due to flatband position)*
- **Demonstration of bandgap tuning using alloy variations**

key recent project results

- **High-quality CGSe films developed with AM1.5 PEC photocurrents of 18 mA/cm^2** *(potential-shift improved over CIGSe, but fill factor worse)*
- **Demonstration of H_2 photo-production at CGSe surface stable for >10 hours**
- **Initial investigation of sulfur incorporation for further favorable band-edge shifts**



CIGSe & CGSe PEC electrodes

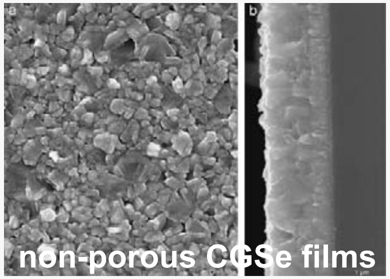


$CuInS_2$ PEC electrodes

Chalcopyrite Path Forward

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 $Cu(In_{(1-x)}Ga_x)(S_ySe_{(1-y)})_2$ alloy- including sulfur
  - graded $CuGaSe_2$ (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**



non-porous CGSe films

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 (>1.6mA/cm^2) met in several films:
    - *3.5 mA/cm^2 demonstrated in low temperature WO_3 films*
    - *>9.0 mA/cm^2 demonstrated in amorphous silicon carbide*
    - *>18 mA/cm^2 demonstrated in copper chalcopyrite films*
  - Conversion efficiency target (2-8% STH) met in HPE devices:
    - *3.1% STH efficiency demonstrated using 2006 WO_3*
    - *4% STH efficiency expected using recent bi-layer WO_3*
  - Stability target (100 hour durability) met:
    - *>100 hour stable operation demonstrated using WO_3*

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

FUTURE WORK

- **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!**