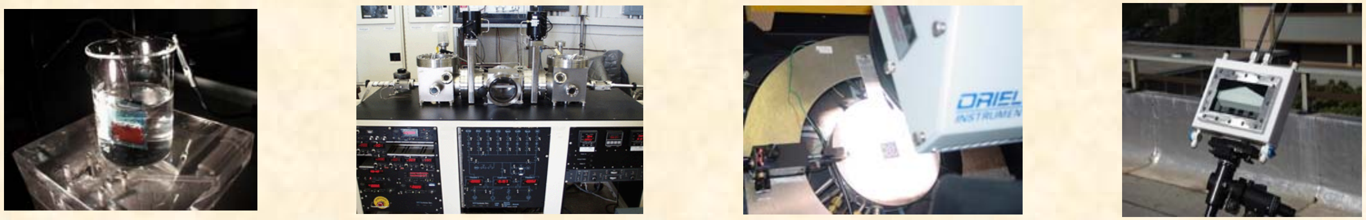


Photoelectrochemical Hydrogen Production: UNLV-SHGR Program Subtask

Robert Perret
University of Nevada Las Vegas
Research Foundation

Eric L. Miller
University of Hawaii at Manoa

15 May 2007

#PDP37

OVERVIEW

Timeline

- **Project start date:** 1 Oct. 2004
- **Project end date:** 31 Dec. 2007
- **Percent complete:** 70%

Barriers

- **Barriers for photoelectrochemical (PEC) H_2 production technologies:**
  - *Y: Materials Efficiency*
  - *Z: Materials Durability*
  - *AB: Bulk Materials Synthesis*
  - *AC: Device Configuration Designs*

Budget

- **Total project funding:** $2.81M
  - *DOE share: $1,685,861*
  - *Contractor share: $1,123,361*
- **FY06 Funding :** $ 958k
- **Funding for FY07:** $0

Collaborators / PIs

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

OBJECTIVES

The primary objective is to assist DOE in the development of hydrogen-production technology utilizing solar energy to photoelectrochemically split water. The primary focus is on low-cost thin film materials (such as metal oxides) and novel multi-junction thin film devices (such as the UH-Hybrid Photoelectrode- *HPE*)

DOE PEC Program Targets

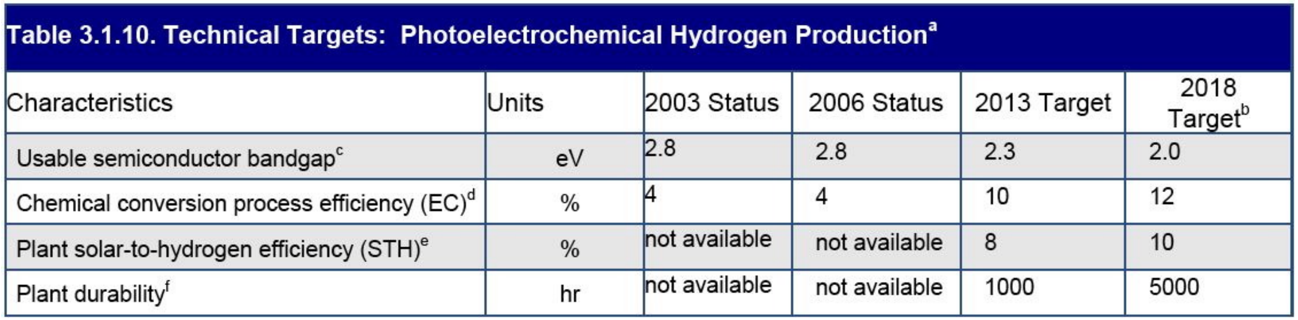
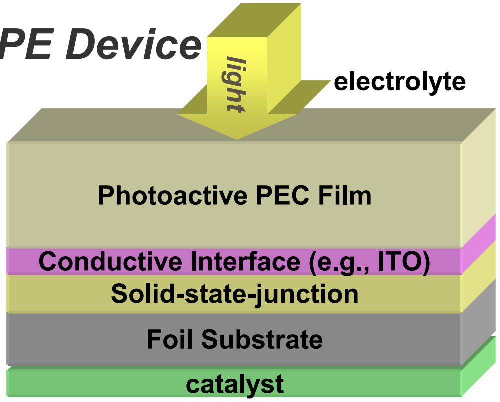


Table 3.1.10. Technical Targets: Photoelectrochemical Hydrogen Production[a]

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

HPE Device



Specific UNLV-SHRG PEC Project Goals

- **Identify and develop new PEC film materials compatible with high-efficiency, low-cost H_2 production devices: Target: 1.6 mA/cm^2 – 6.5 mA/cm^2 AM 1.5 photocurrent**
- **Demonstrate functional multi-junction device incorporating best-available PEC film materials: Target: 2 - 8 % STH efficiency under AM 1.5 illumination**
- **Develop avenues, integrating new theoretical, synthesis and analytical techniques, for optimizing future PEC materials and devices**
- **Explore avenues toward manufacture scaled devices and systems**

General Approach Philosophy

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.

➢*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

➢*Application to Focus Materials:*

●W-compounds ●Zn-compounds ●Fe-compounds ●Si-compounds ●Cu-chalcopyrites

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

SUMMARY

PROGRESS

- **Collaborative Research Team Established:** *combining materials theory, synthesis and characterizations, to expedite the materials discovery and development process for improved PEC devices.*
- **Critical Experience, Protocols, and Infrastructure Developed:**
  - *Versatile synthesis tools established for fabricating PEC materials & devices*
  - *Comprehensive characterization protocols established for PEC materials & devices*
  - *Rapid-throughput synthesis & screening techniques developed to facilitate discovery*
  - *Manufacture scale process demonstrated for HPE device fabrication*
- **Focus Materials Classes Established:** *including WO_3-, ZnO- Fe_2O_3-, silicon- , and copper chalcopyrite-based thin films.*
- **Key Targets Met in Focus Materials Experiments:**
  - *Photocurrents in excess of 3 mA/cm^2 in tungsten-based compound films*
  - *Photocurrents in excess of 6.5 mA/cm^2 in Si- and chalcopyrite-based films (with additional bias constraints to be corrected in band edge alignment modifications)*
  - *STH Device efficiencies in excess of 3% in WO_3-based multijunction structures under 1 sun*

FUTURE

- **Continued Development of Research Team Capabilities and Collaboration**
- **Continued Optimization of Performance and Durability in Focus Materials**
- **Continued Discovery of New Materials and Possible Down-Selection of Old Materials**
- **Selection of Best Materials for Incorporation in High-Efficiency PEC Devices**

Approach: Theory

Theoretical modeling of PEC materials:

- To provide theoretical guidance and understanding on materials studied by the PEC team
- To search for new materials and new concepts

Background of Density-Functional Theory (DFT):

$$-\frac{h^2}{8\pi^2 m}\nabla^2\psi_j(r)+V_{eff}(r)\psi_j(r)=\varepsilon_j^{KS}\psi_j(r)$$ K-S equation

$$V_{eff}(r)=V_H(r)+V_N(r)+V_{XC}(r)$$

$V_{XC}(r)$: *Exchange-correlation potentials: LDA, or GGA*

Applications:

Total energies, Electronic structures such as band structure and density of states, Optical properties such as optical absorption coefficient and transition properties

Approach: Theory

Specific Applications in PEC Materials

Collaboration on WO_3 with the PEC team:

- Determined conduction and valence band positions for cation and anion doped WO_3
  - Nitrogen incorporation leads to bandgap reduction in WO_3
  - Calculated optical absorption coefficient for WO_3:N
  - Calculated a minimal shift for the conduction band minimum with molybdenum doping.

Results on ZnO:

- N-incorporation leads to bandgap reduction in ZnO
- Ga-N cluster doping may form intermediate band in ZnO
- Group-IB elements (Cu, Ag, Au) lead to VBM up shift in ZnO
- p-type and gap reduced ZnO is possible by Cu and Ag incorporation
- Ga-N cluster doping may form intermediate band in ZnO

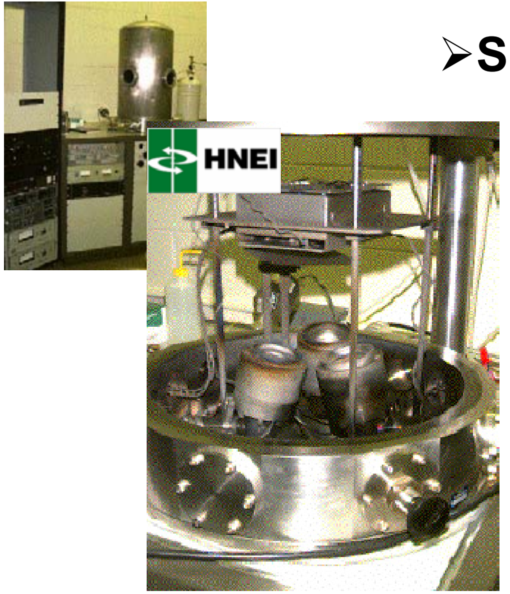
New Materials:

- Theoretical results from WO_3 and ZnO to be included in modeling of new PEC material systems

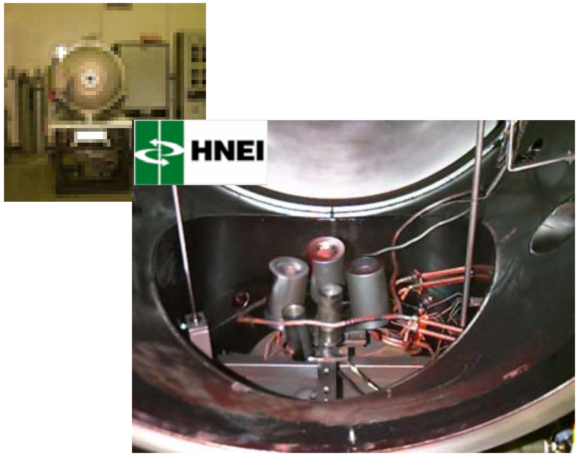
Approach: Synthesis

Collectively, our team commands a broad portfolio of thin film synthesis techniques to facilitate the discovery and development of PEC materials and devices for high-performance, low-cost hydrogen production systems, including. Team synthesis capabilities include:

- **Physical Vapor Deposition Systems**
- **Chemical Vapor Deposition Systems**
- **Spray Pyrolysis Fabrication Systems**
- **Sol-Gel Fabrication Systems**



Reactive sputtering system for compound material films (including oxides, sulfides, etc.)



Co-Evaporation system for copper chalcopyrite films (CIGS, CGS, etc.)

Plasma-enhanced CVD system for low temperature synthesis of metal oxide films

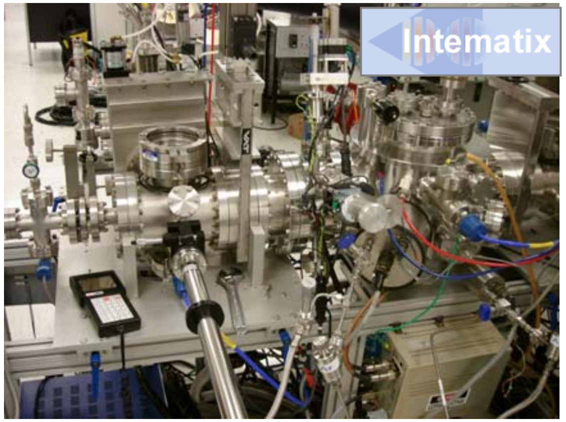
Approach: Synthesis

The team also offers a range of advanced techniques to facilitate rapid discovery of new materials classes and the establishment of large-scale device fabrication. Specific combinatorial synthesis and manufacture-scale equipment includes:

- **Combinatorial Synthesis Systems**
  - –Automated Pyrolysis systems
  - –Automated Physical-Vapor-Deposition systems

- **Manufacture-Scale Film Technology**
  - –Large-scale vacuum-system cluster tools
  - –Cassette systems for large sheet depositions

Automated combinatorial pyrolysis system



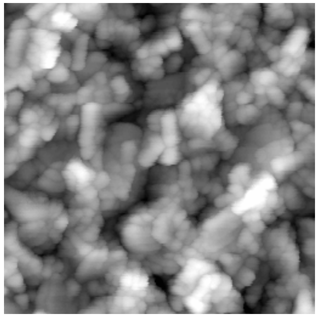
Automated combinatorial physical-vapor-deposition system

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

Approach: Characterizations

Materials Properties

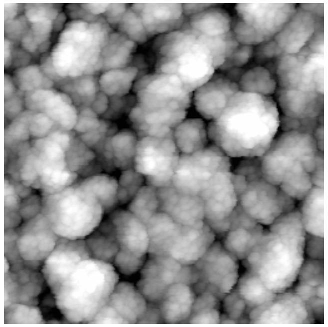
- **Morphology: Scanning Electron Microscopy, Atomic Force Microscopy, Spectroscopic Ellipsometry**



AFM of WO_3 Films

←Pure WO_3

N_2-doped WO_3→



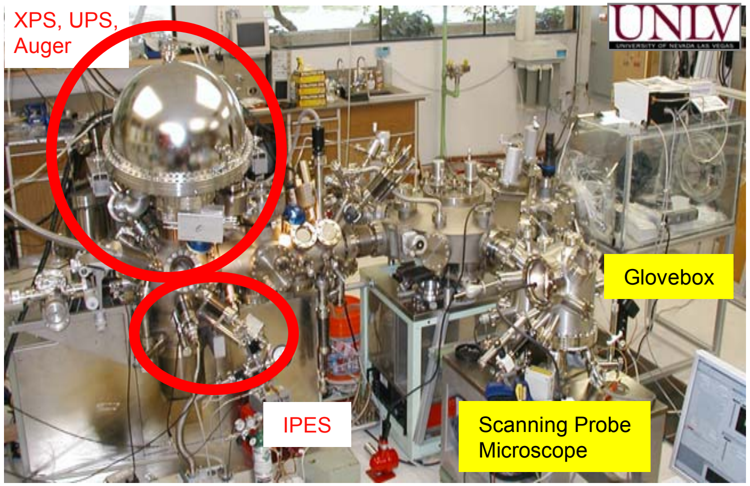
- **Microstructure: X-Ray Diffractometry, EBSD, Transmission Electron Microscopy**
- **Chemistry: Secondary Ion Mass Spectrometry, X-ray Photoelectron Spectroscopy, Synchrotron X-ray Emission and Absorption Spectroscopy**

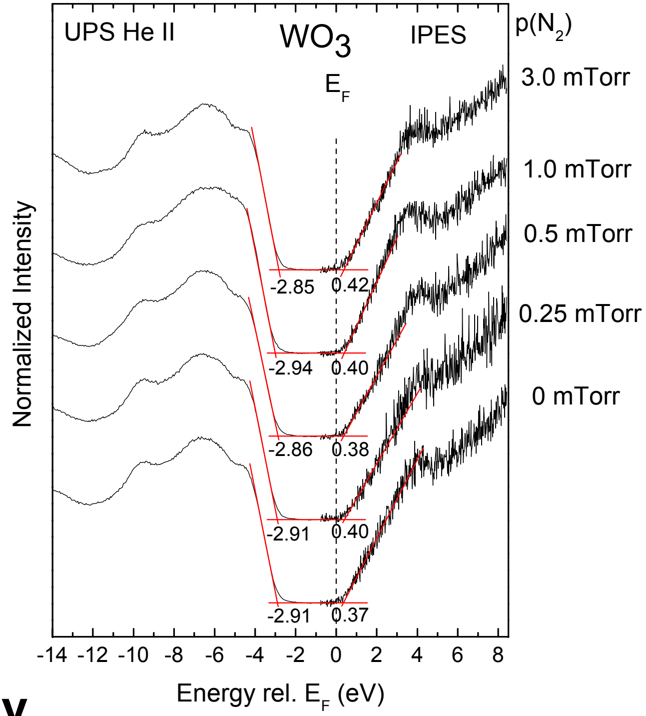
Approach: Characterizations

Electronic Structure

Electronic Surface Bandgap, Band Edges, Band Alignment, Fermi Energy, Work Function, Electrical Properties

- **UV Photoelectron Spectroscopy, Inverse Photoemission**





- **Impedance Spectroscopy, UV-Vis Spectroscopy**

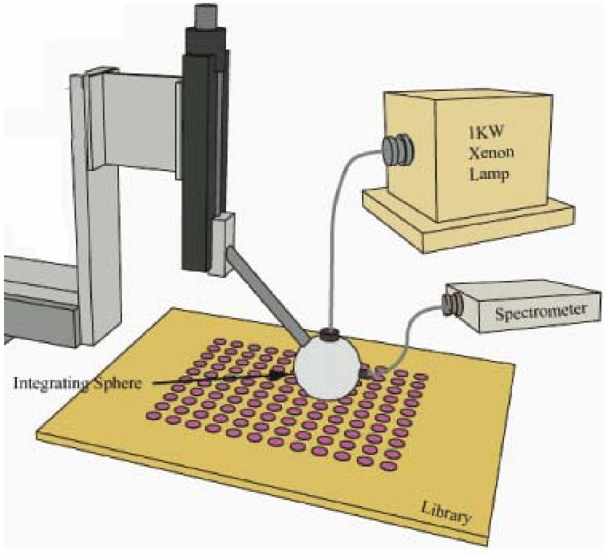
- **Conductive Atomic Force Microscopy, Scanning Kelvin Probe Microscopy, Scanning Tunneling Spectroscopy**

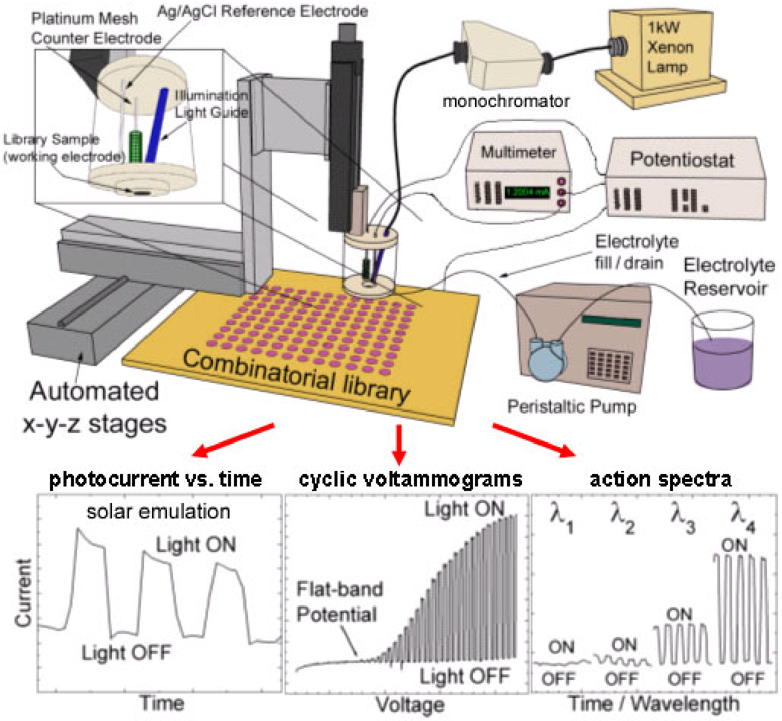
Approach: Characterizations

Optical and Photoelectrochemical Properties

- **Optical-Photoelectrochemical Combinatorial Screening Systems**

Diffuse Reflectance Spectrometry





- **Solar Cell I-V Curve Testing System, Solar Cell Spectral Response Measurement System**
- **Photoluminescence and Cathodoluminescence**

Specific Approach: Focus Materials

Our team utilizes its collective expertise and capabilities in theoretical materials modeling, in materials synthesis, and in materials screening and characterization to identify and develop an expansive set of promising PEC thin-film materials classes. The five classes of "focus materials" currently under investigation include:

- **Tungsten-Based Compound Films (U. Hawaii, Intematix)**
  - Modified Tungsten Oxide Compounds with Anion/Cation Substitutions
- **Zinc-Based Compound Films (NREL)**
  - Modified Zinc Oxide Compounds with Anion/Cation Substitutions
- **Iron-Based Compound Films (UCSB, Altair Nano)**
  - Novel Iron-Based Compound Materials, including Fe_2O_3 Nanorods
- **Silicon-Based Compound Films (MVSystems)**
  - Amorphous Silicon Carbide Films with p- and n- type Doping
- **Copper Chalcopyrite Compound Films (U. Hawaii)**
  - Copper-Indium-Gallium-Selenium-Sulfur Compounds

Progress: Tungsten-Based Compound Films

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

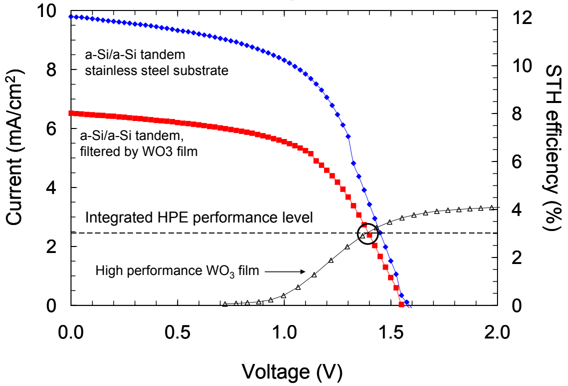
promise

- Sufficient absorption to generate modest photocurrents
- Good electron transport properties
- High Stability in Electrolytes
- Thin film process scalable
- Demonstrated in prototype multi-junction devices.

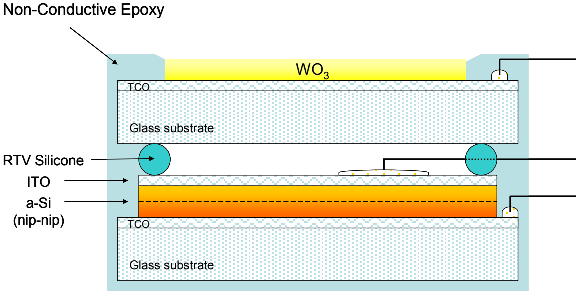
challenges

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

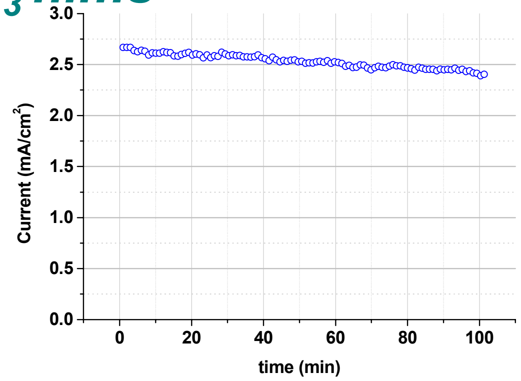
Hybrid Photoelectrode with pure WO_3 films



Load Line Analysis



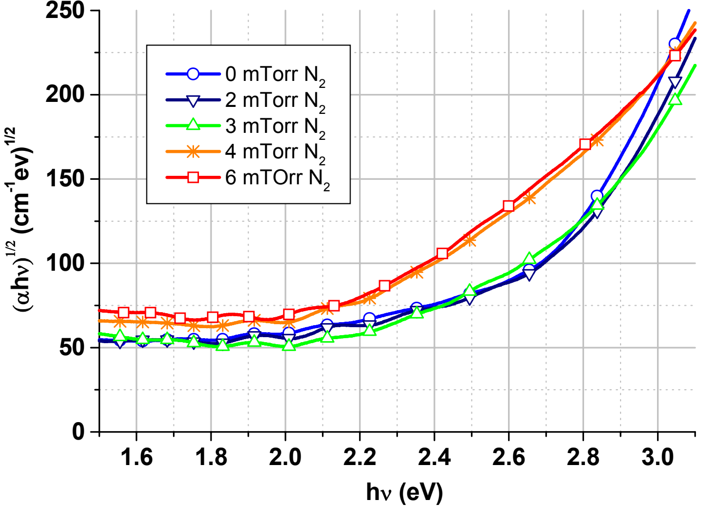
Device Configuration



Performance

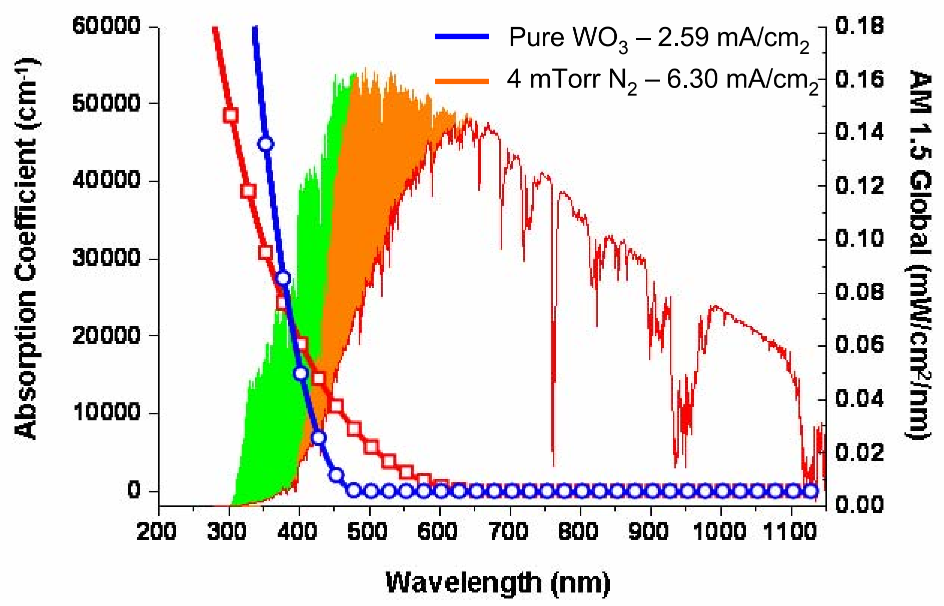
Progress: Tungsten-Based Compound Films

UV edge plotted as indirect bandgap

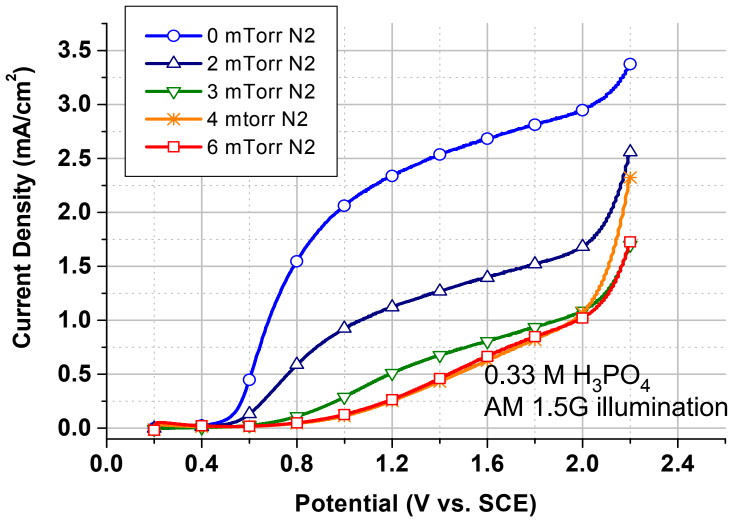


Calculated current density based on UV absorption edge for a 1 μm thick film

Shaded region represents absorbed portion of AM1.5G



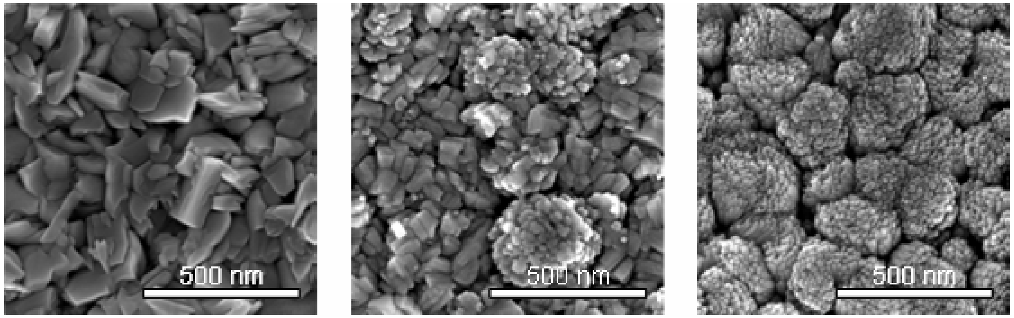
PEC testing of WO_3:N

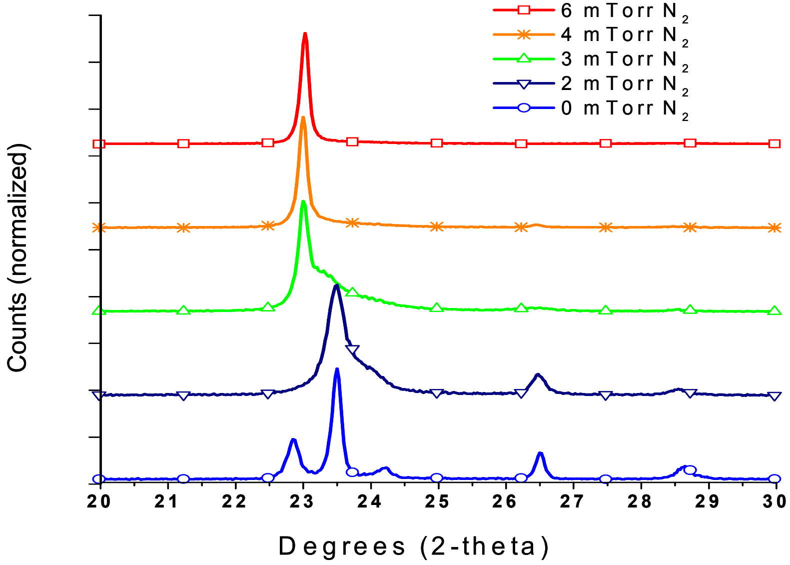


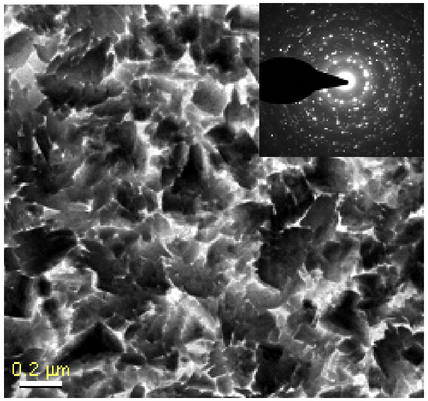
With sufficient nitrogen in the sputtering ambient, bandgap reductions are realized, however this increase in absorption does not correlate with an increase in measured photocurrents . . .

Progress: Tungsten-Based Compound Films

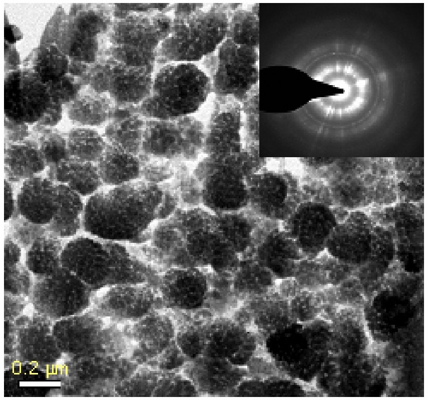
Influence of Nitrogen on Structure







Highly crystalline WO_3



Nitrogen doped WO_3

X-ray diffraction pattern shows an initial decrease in crystallinity for monoclinic phase followed by transformation to a stabilized cubic phase for nitrogen partial pressures greater than 3mTorr. The TEM diffraction pattern for nitrogen doping shows smearing, indicating a highly defective lattice.

Path Forward: Tungsten-Based Films

SUMMARY

- Tungsten oxide has been demonstrated in a multi-junction hybrid phototelectrode configuration.
- Nitrogen is observed to reduce the bandgap to ~2 eV.
- Incorporation of nitrogen results in a highly defective lattice. This degrades the transport properties resulting in poor PEC performance.
- Theory indicates that other dopants can favorably alter band edges.

FUTURE WORK

- Elimination of lattice defects for the nitrogen doped WO_3
  - by adjusting sputtering parameters
  - by post sputtering annealing
  - by exploring quaternary systems
- Pursue bandgap reduction using different anion/cation species
  - oxy-sulfides (in addition to the oxy-nitrides)
  - by metallic cations
- Based on the need to minimize requisite bias voltage, we will investigate valence band modifications, as well as the effect of composition on conduction band level and its alignment with the hydrogen reduction potential.

Progress: *Zinc-Based Compound Films*

ZnO is inexpensive, nontoxic, and easy to synthesize. It also has a direct bandgap and high electron mobility thereby making it a good candidate for PEC splitting of water.

promise

- **Conduction band edge only slightly mismatched to drive the hydrogen reaction.**
- **Impurity doping can shift the valence band edge, providing for bandgap reduction.**
- **Can also fabricate as P-type ZnO**

challenges

- **Bandgap is too large to effectively utilize the visible light**
- **Requires stability improvement against photocorrosion**

strategies for PEC improvement

Bandgap reduction

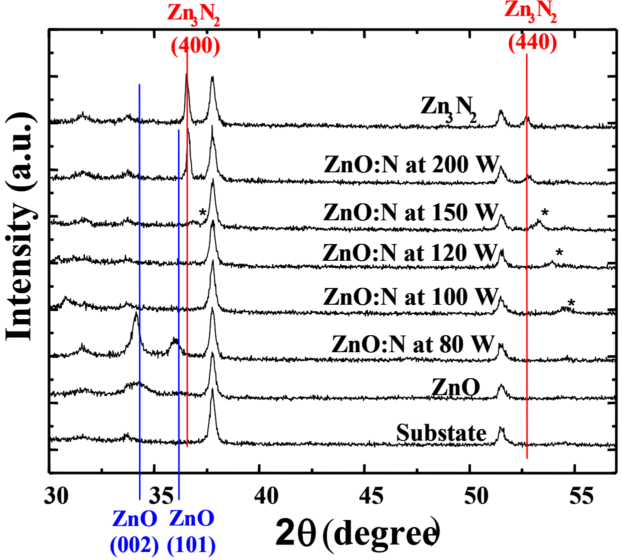
- **Impurity doping using anion or cation species**

Explore p-type ZnO

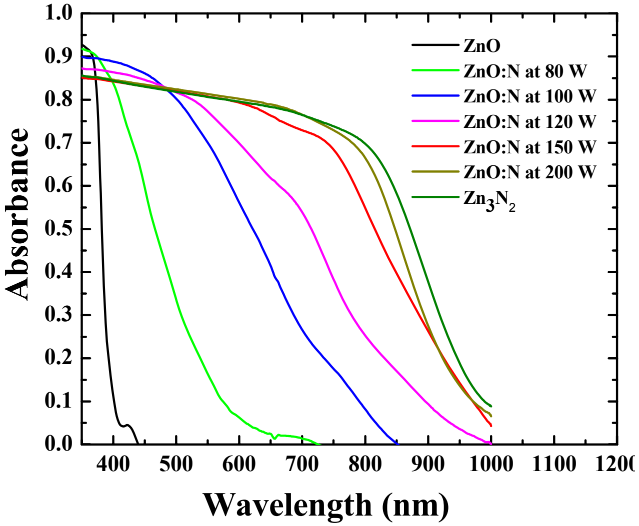
- **Impurity doping using group 1B metals**

Progress: Zinc-Based Compound Films

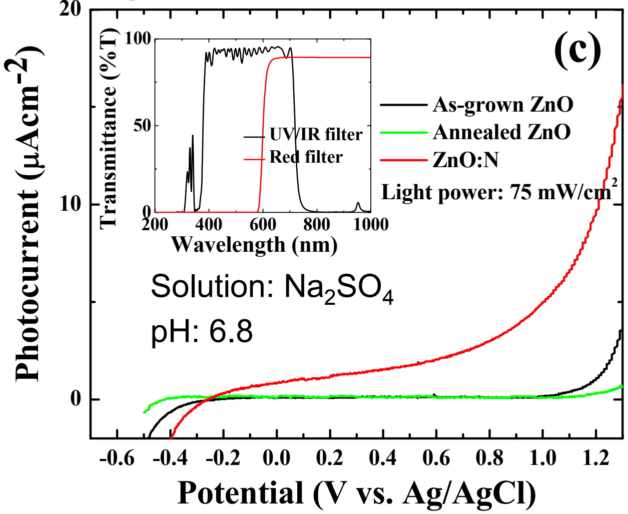
Structural evolution for RF sputtering of ZnO:N



Optical absorption spectra from ZnO:N samples



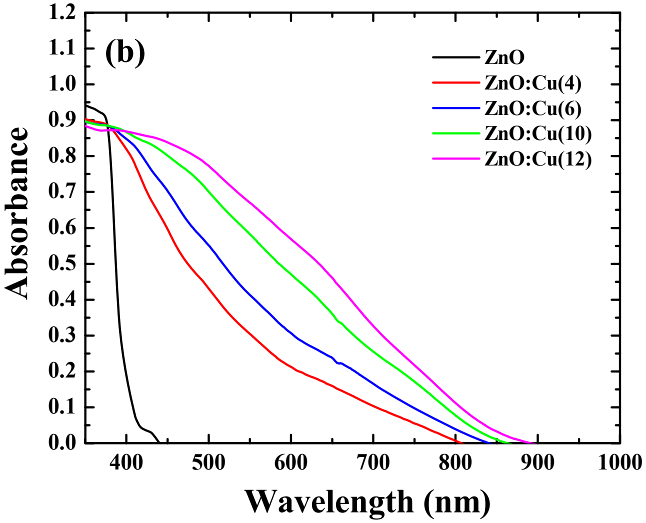
Photocurrent-voltage curves of the samples under light illumination with the UV/IR filter



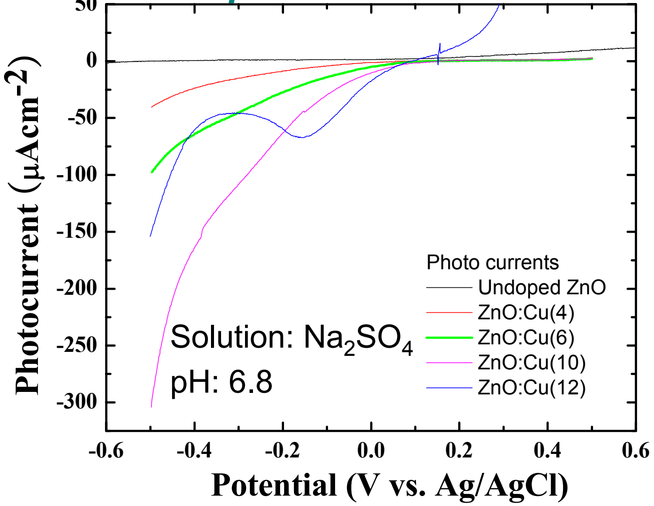
- **High quality pure ZnO thin films are synthesized**
- **N-incorporation into ZnO thin films was achieved**
- **Bandgap reduction in ZnO thin films was achieved by N-incorporation**
- **Photo-response in ZnO:N thin films was demonstrated**

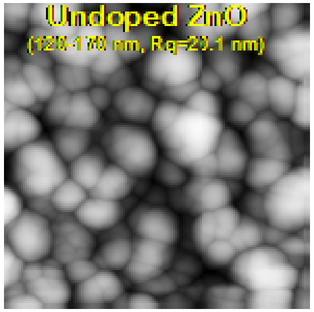
Progress: Zinc-Based Compound Films

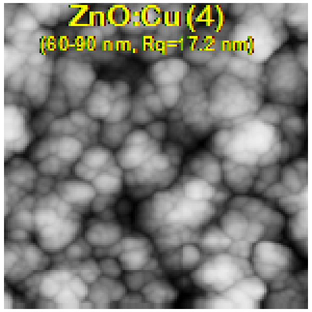
Optical absorption spectra from ZnO:Cu samples

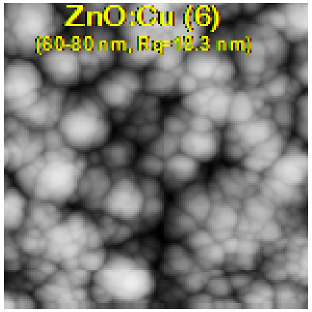


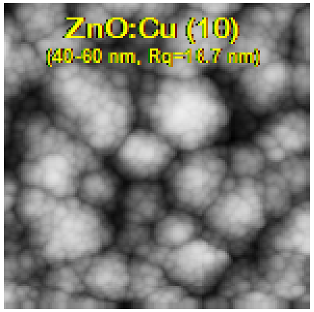
Photocurrent-voltage curves of p-type ZnO:Cu samples

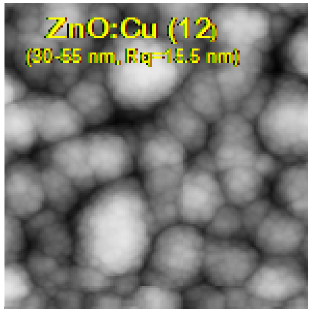












Cu increase → Grain size and surface roughness decreased

- **Bandgap reduction in ZnO thin films was achieved by Cu-incorporation**
- **P-type ZnO thin films with reduced bandgaps were achieved by Cu incorporation**
- **Photo-response in ZnO:Cu thin films was demonstrated**

Path Forward: Zinc-Based Compound Films

SUMMARY

- Preliminary work shows that nitrogen can be effectively incorporated into ZnO films to reduce bandgap
- Need to improve crystallinity for ZnO:N to realize good PEC properties.
- Theoretical calculations show that doping with group 1B transition metals (Cu, Ag) results in bandgap reduction.
- Cu was incorporated into ZnO films with mixed results – bandgap reduction is observed and Cu is found at Zn sites for select films, however the measured photocurrents are low.

FUTURE WORK

- The process for RF sputtering of ZnO films requires optimization.
    - Study the film growth as a function of substrate temperature.
    - Incorporation of impurity dopants via co-sputtering will be employed.
- Band gap reduction
    - Impurity band generation by new impurities
    - Acceptor-donor co-doping
- Stability improvement

Progress: Iron-Based Compound Films

Iron Oxide, as a commonly-found material with bandgap well-suited for the direct solar water splitting of water, is considered the "Holy Grail" of PEC materials- but its performance has been severely limited by opto-electronic properties…

promise

- Bandgap ~ 2 eV (40% solar light absorption).
- Abundant and inexpensive
- High Stability in Electrolytes (pH>3)

challenges

- Carrier Transport
- Valence Band Edge
- Water Oxidation Kinetics
- Low optical absorption

strategies for PEC improvement

Photon To Electron Conversion Increase

- Growth of crystalline oxide
- Direct growth along the preferred electron conduction paths
- High Surface Area Materials

Shift of Band positions

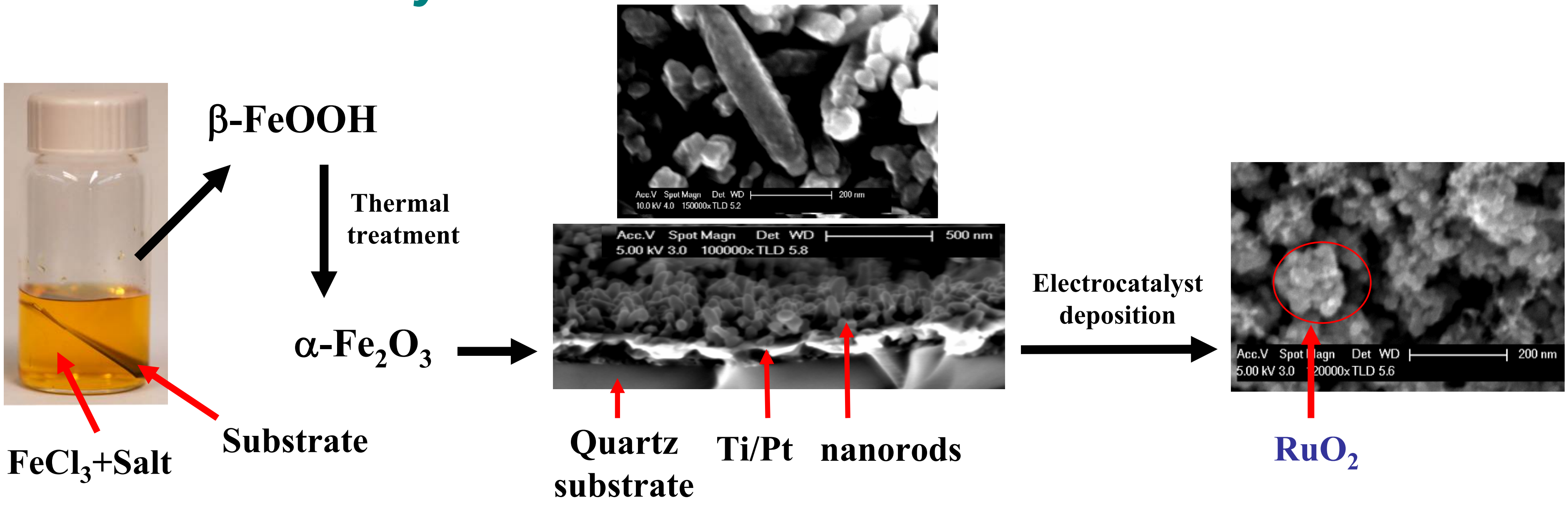
- Quantum size effects
- Transition metal doping

Improve Kinetics of Water Oxidation

- Identify and deposit optimized surface oxidation electro-catalyst

Progress: *Iron-Based Compound Films*

Synthesis of nanorod electrodes



β-FeOOH

Thermal treatment

α-Fe_2O_3

Electrocatalyst deposition

$FeCl_3$+Salt

Substrate

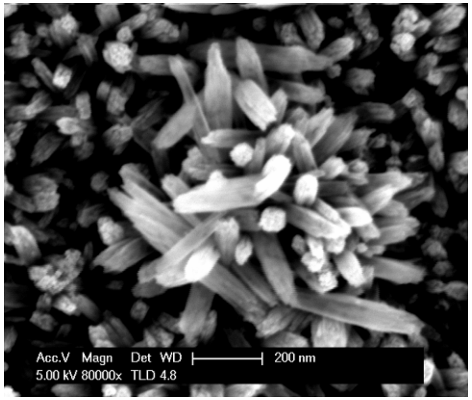
Quartz substrate

Ti/Pt

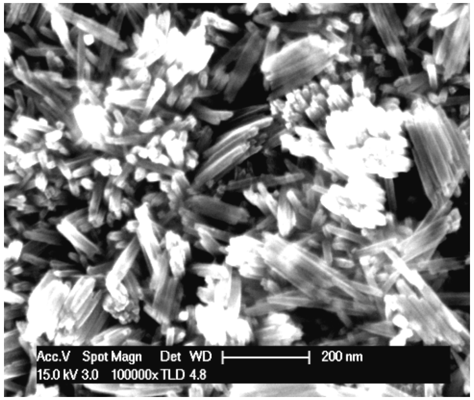
nanorods

RuO_2

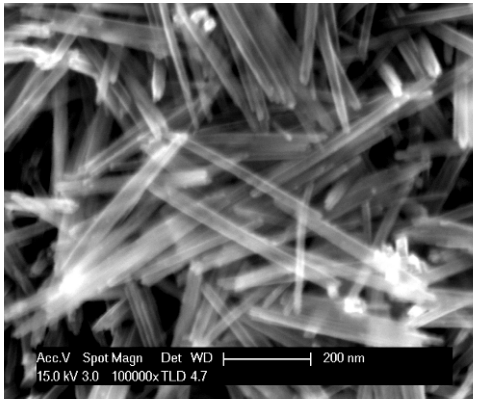
Synthetic control of nanorod structure



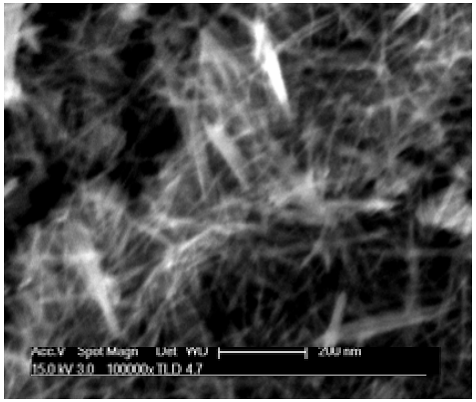
1) 35 ± 3 nm



2) 21 ± 2 nm



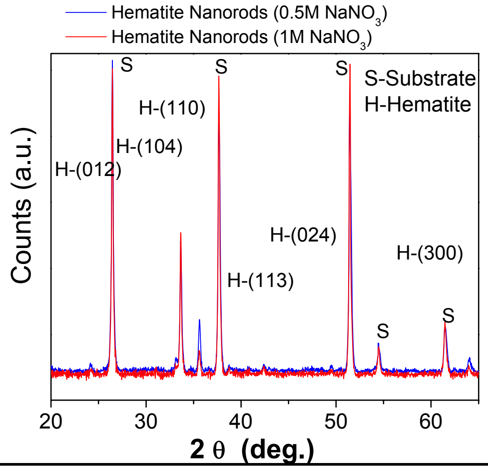
3) 20 ± 3 nm

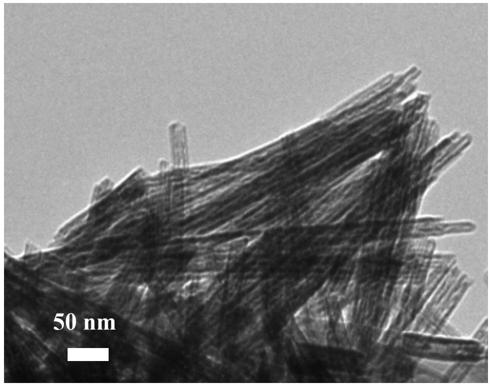


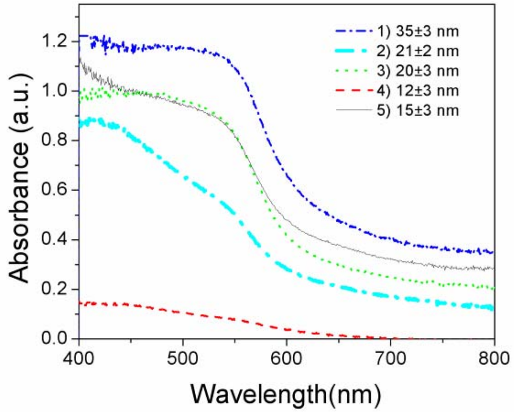
4) 12 ± 3 nm

Progress: Iron-Based Compound Films

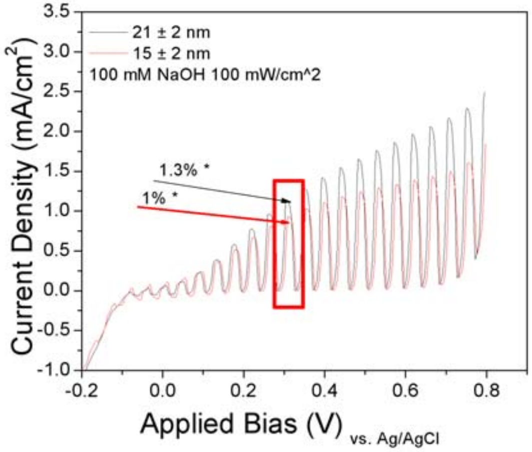
Nanorod characterization & performance







1)



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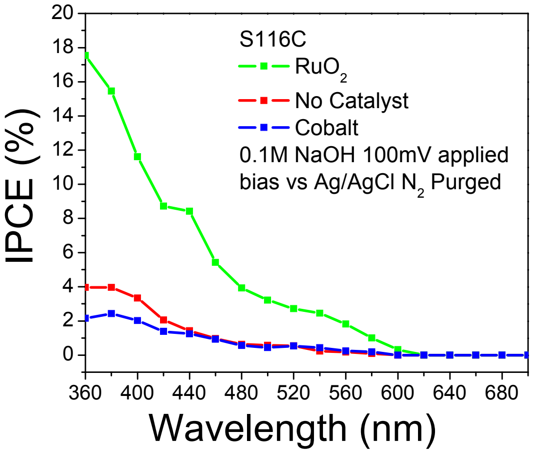

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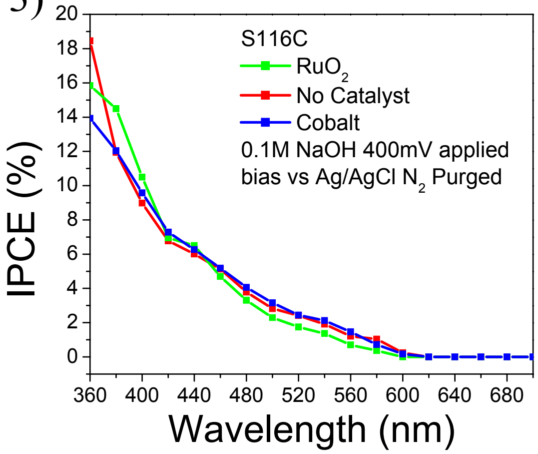


1) Photoelectrochemical performance of 21 and 15 nm nanorods under applied bias showing and efficiency of 1.3% and 1% respectively. (2,3) IPCE of 35nm Fe_2O_3 nanorods with an applied bias of 100mV and 400mV, graph 2 and 3 respectively, showing the dramatic improvement of the nanorods with the electrodeposition of RuO_2 at low applied bias while at high applied bias the oxygen evolution catalyst is not improving the performance of the nanorods. 4) Table of results showing the Efficiency of the nanorods from graph 2 and 3.

* Efficiency from IPCE data

4)

	Applied Bias	
	100 mV	**400 mV**
No Catalyst	**0.3%**	**1.0%**
RuO_2	**1.6%**	**0.9%**
Cobalt	**0.2%**	**1.0%**

Path Forward: *Iron-Based Compound Films*

SUMMARY

Early stages of research and development on iron oxide nanorods synthesis have shown:

- Control over the size and morphology of the nanostructures
- Improved photoelectrochemical performance as compared with spray pyrolysis deposited films
- Photoelectrochemical efficiencies of ~1 %

- This synthesis method is applicable to wide variety of substrates and can be adapted to any size of substrates.

FUTURE WORK

- **Control gross structure of photocatalysts**
  - Nanorod synthesis conditions (pH, T, electrolyte composition)
  - Explore use of framework templates (deposit in cubic phase nanopores)
- **Control opto-electronic properties**
  - Nanorod size reduction to increase VB Confinement at d<6nm
  - Nanorod growth to be along (110) plane
  - Nanorod doping by *in situ* growth or high temperature diffusion
- **Control kinetics**
  - Selective deposition of surface electrocatalysts (start with Pt, Ni, Au, Ru)

Progress: Silicon-Based Compound Films

Amorphous silicon carbide is an electrochemically stable and photoactive material with tunable bandgap, which would enable the fabrication of "all-silicon" multi-junction water-splitting devices.

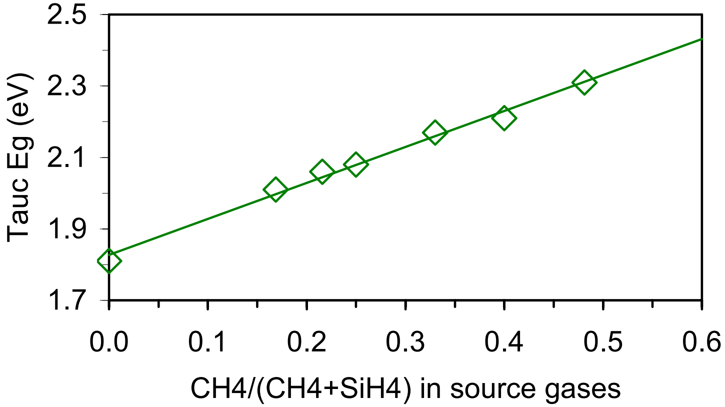
promise

- Tunable bandgap of 2.0-2.3 eV and good optoelectronic quality
- Large knowledgebase from a-Si technology
- a-SiC shows good corrosion resistance
- Enables "all-silicon multi-junction device" to be fabricated in a "cluster tool" machine

challenges

- 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 by carbon content (Gas flow ratio)

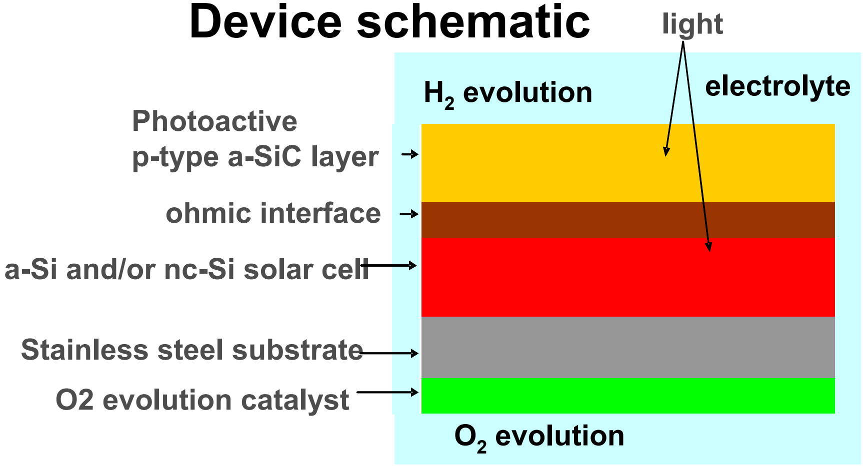


Amorphous Si Panel

Progress: Silicon-Based Compound Films

All-Silicon Hybrid PEC Device Designs

Device schematic


light

H_2 evolution

electrolyte

Photoactive p-type a-SiC layer

ohmic interface

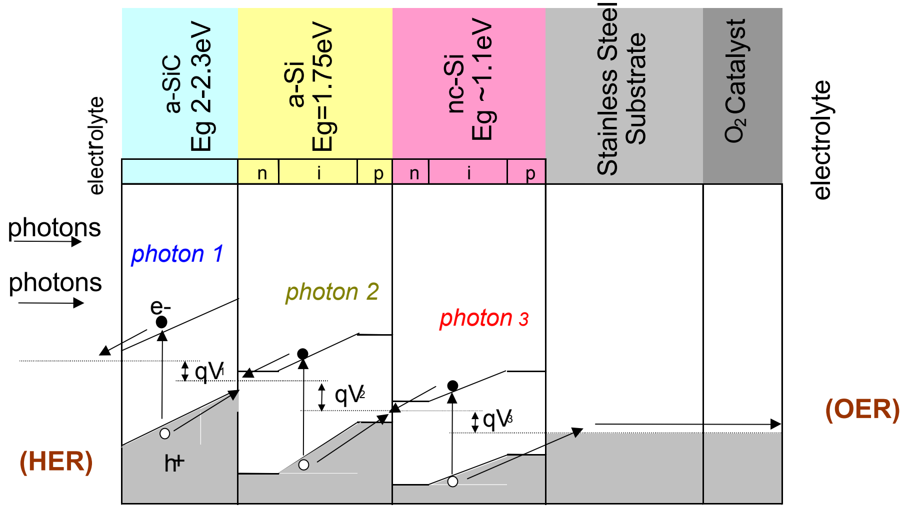
a-Si and/or nc-Si solar cell

Stainless steel substrate

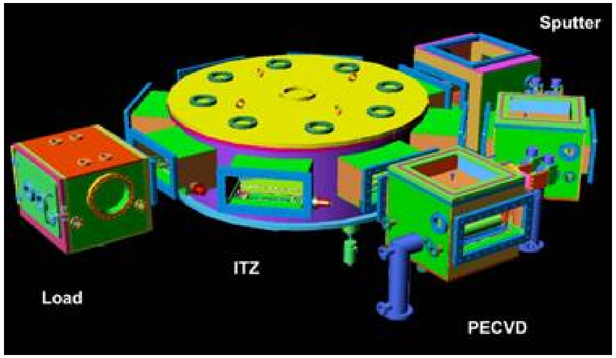
O2 evolution catalyst

O_2 evolution

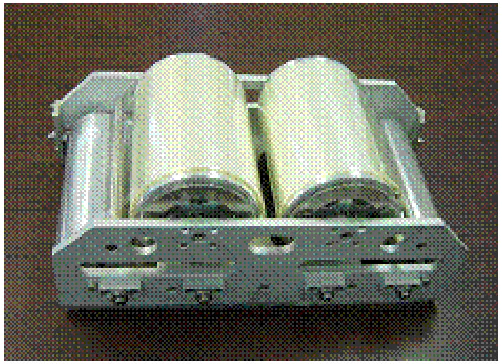
Band diagram using A-Sic PEC film



Cluster-tool fabrication equipment



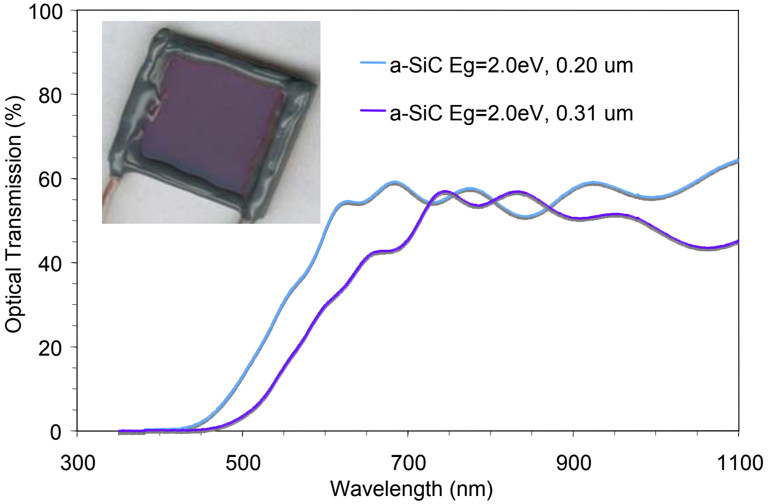
large-scale cluster tool design


reel-to-reel cassette*

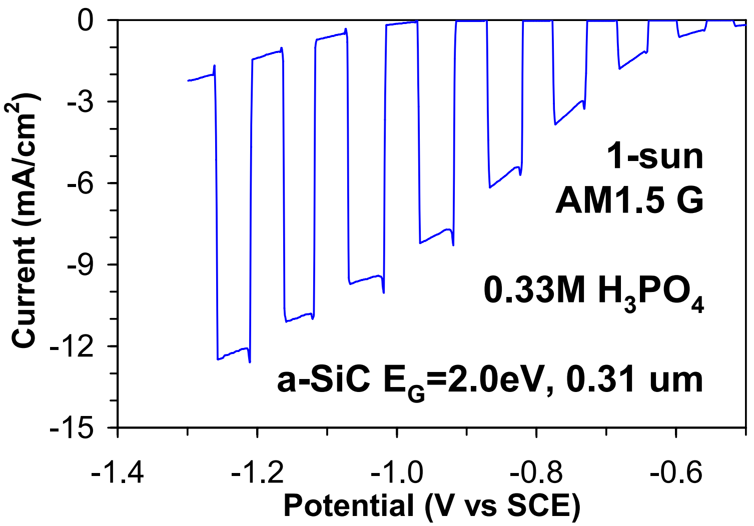
* US patent #6,258,408B1: **MVSystems**

Progress: Silicon-Based Compound Films

Optical properties tailored through bandgap and thickness



Photocurrent of >9mA/cm^2 with a-SiC photocathode



Route to >10% STH Efficiency

photo-electrode	photo-electrode bandgap (eV)	current available (mA/cm2)	photovoltaic layer configuration	current available (filtered by top layer) (mA/cm2)	possible STH (%)	achieved STH to date(%)
WO_3	2.6-2.8	4.3-3.3	a-Si/a-Si	8.0	5.3	**3.1**
SiC	2	14.4	a-Si/nc-Si	6.0	7.4	
SiC	2.35	8.1	a-Si/nc-Si	7.8	**~10**	
SiC	~2	~14	nc-Si	~14	**~17**	

Path Forward: Silicon-Based Compound Films

SUMMARY

- One-sun photocurrent of ~9 mA/cm^2 demonstrated for a-SiC electrode
- a-SiC films appear stable in cathodic regime (short-term tests)
- Flatband potential and photocurrent onset indicate non-ideal valence band maximum position and kinetic limitations
- a-SiC is compatible with automated fabrication of multijunction devices in cluster tool deposition machine

FUTURE WORK

- Optimize optoelectronic quality of a-SiC at E_G=2.0eV-2.3eV
  - systematic variation of PECVD process parameters
- Comprehensive PEC characterization a-SiC photoelectrodes
  - band positions, electrode kinetics
  - long term stability
- Fabricate and characterize complete monolithic a-SiC/a-Si multijunction PEC device

Progress: Copper Chalcopyrite Films

Cu(In,Ga)Se$_2$ is proven as an efficient absorber for thin-film solar cells and its optoelectronic properties are equally well suited for photoelectrolysis.

promise

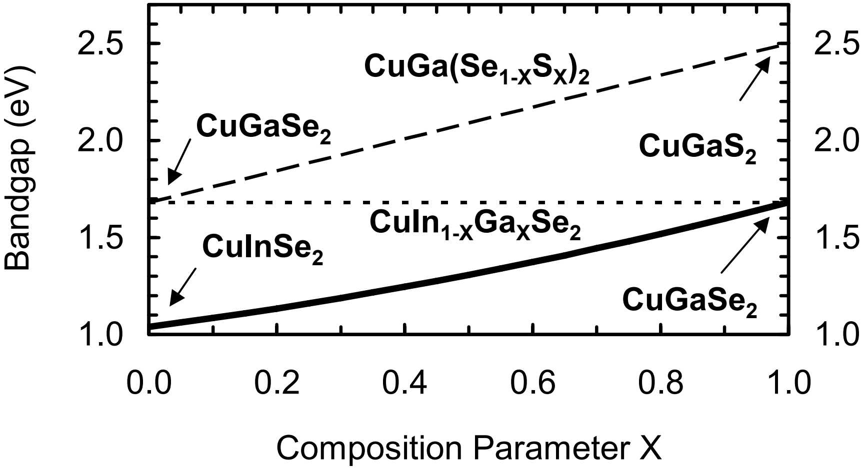
- **Direct bandgap and good carrier transport properties**
- **High PEC photocurrents demonstrated for p-type Cu(In,Ga)Se$_2$ electrodes**
- **Bandgap and band edges "tunable" by composition**
- **Synergy with PV CIGS multijunction device research and development**

challenges

- **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 Bowing Ranges of Cu(In,Ga)Se$_2$ and CuGa(Se,S)$_2$

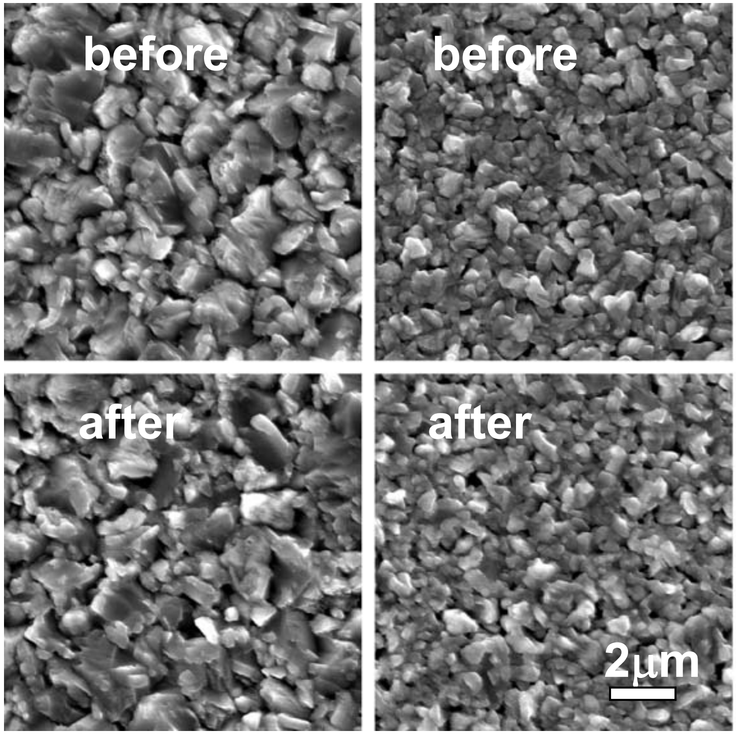
S.-H. Wei and A. Zunger, JAP 78, 3846 (1995);
H. Matsushita et. al, JJAP 29, 484 (1990)



Progress: Copper Chalcopyrite Films

Stability, and Band Edge Positions

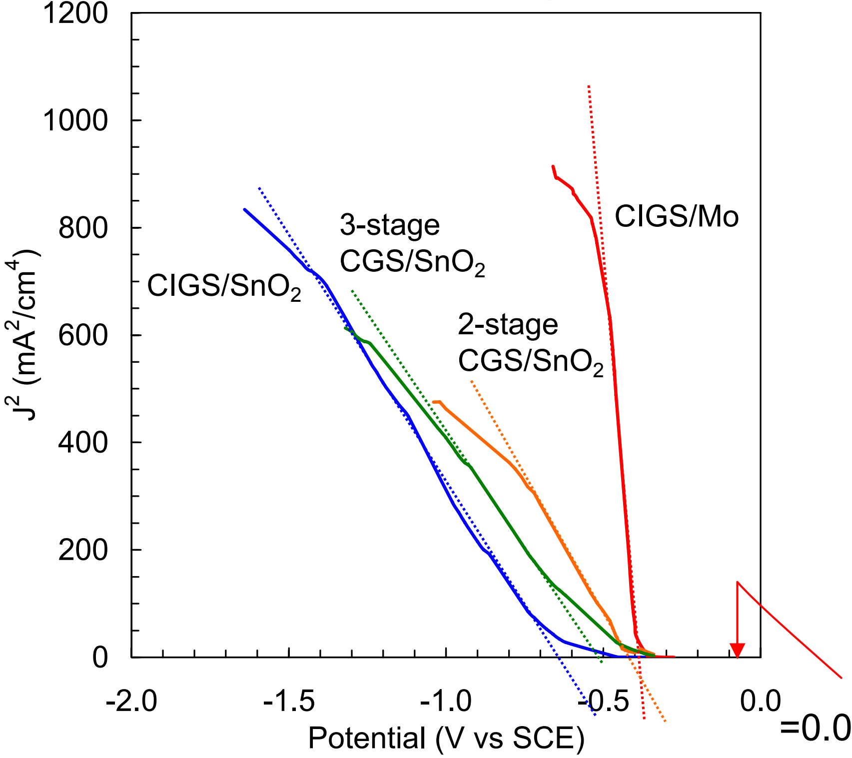
Stability: morphology before/after PEC testing



$CuIn_{0.2}Ga_{0.8}Se_2$
(3-stage process)

$CuGaSe_2$
(3-stage)

Photocurrent onset potential

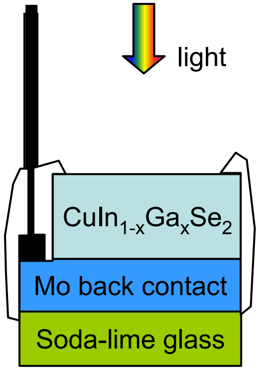


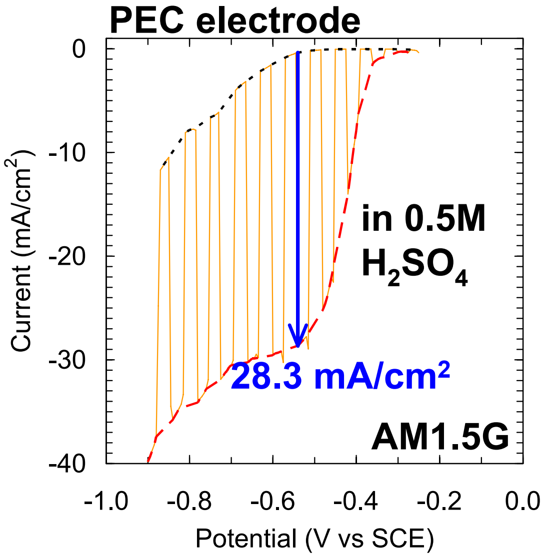
CIGS/Mo:
Illuminated
open-circuit
=0.07 V vs SCE
=0.31 V vs NHE

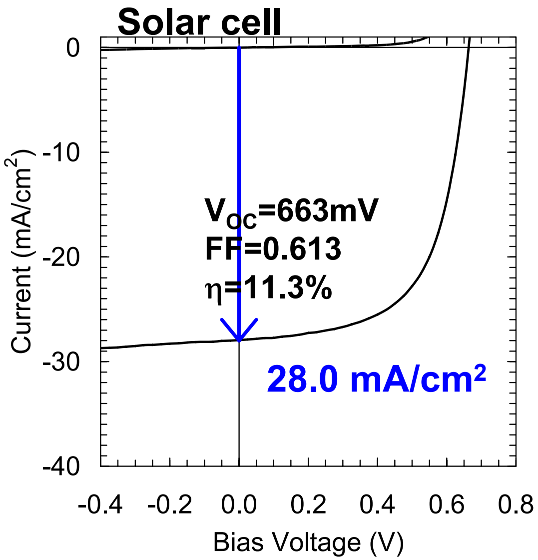
- **Electrodes are stable during short-term PEC testing**
- **Valence band edge too positive in current samples – high bias required**
- **Photocurrent onset at least 0.3V more cathodic than flatband potential**
- **Resistance of back contact (high/SnO_2:F vs low/Mo) has strong impact on photocurrent curve**

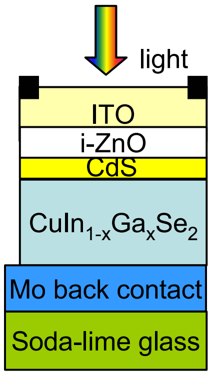
Progress: Copper Chalcopyrite Films

1-Sun Photocurrent: similar in PEC and PV Devices ($CuIn_{0.4}Ga_{0.6}Se_2$)

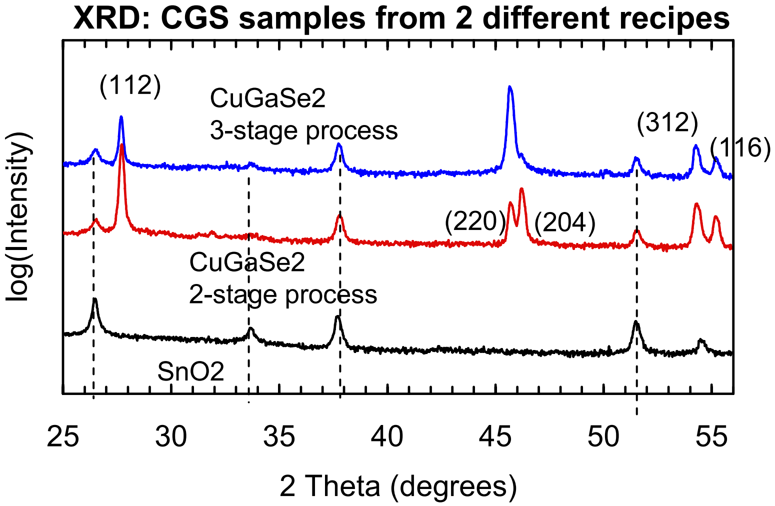


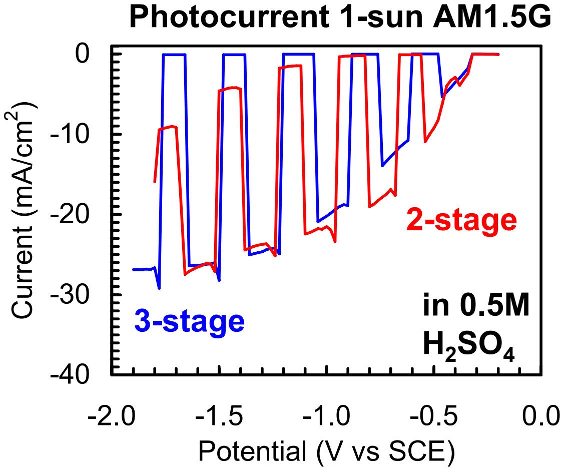






$CuGaSe_2$ deposition conditions, film texture, and photocurrent curves





Preliminary data shows possible effect of texture [(112)/(220)+(204)] on saturation photocurrent and dark current.

Path Forward: Copper Chalcopyrite Films

SUMMARY

- 1-sun photocurrents of 21-28 mA/cm^2 demonstrated for wide-bandgap CIGS and CGS electrodes
- Wide-bandgap CIGS and CGS Films appear stable in cathodic regime
- Flatband potential measurement indicates valence band maximum too high
- Late photocurrent onset indicates kinetic limitations at electrode surface

FUTURE WORK

- Assemble comprehensive body of PEC data on existing CIGS electrodes
- Study materials with wider bandgap and lower valence band
  - $CuGaSe_2$ with Cu-poor surfaces
  - Alloy with sulfur for wider bandgap $CuGa(Se,S)_2$
- Explore metal nanoparticle deposition on electrode surface for kinetic improvements