Characterization of Materials for Photoelectrochemical Hydrogen Production (PEC)

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Project ID #
PD051

This presentation does not contain any proprietary, confidential, or otherwise restricted information

Overview

Timeline

- Project start date: 5/6/08
- Project end date: 5/5/10 (no-cost extended; further extension to 5/5/11 in negotiations)
- Percent complete: 100% (67% if extended)

Budget

- Total project funding
  - DOE share: $200k (FY08/09)
  - Contractor share: $50k
- Funding received in FY09: none (no-cost extension)
- Funding for FY10: $100k (in negotiations)

Barriers

- Barriers addressed
  - H. System Efficiency
  - Lifetime
  - Indirectly: G. Capital Cost

Partners

- Interactions/collaborations: DOE EERE PEC WG (NREL, HNEI, MVSystems, UCSB, Stanford, LLNL), Berkeley Lab, HZB Berlin, U Würzburg
- Project lead: C. Heske, UNLV

Activity Overview: Electronic and Chemical Properties of PEC candidate materials *(Relevance)*

To enhance understanding of PEC materials and interfaces and promote break-through discoveries:

- Utilize cutting-edge soft x-ray and electron spectroscopy characterization
- Develop and utilize novel characterization approaches (e.g., *in-situ*)
- **Address materials performance, materials lifetime, and capital costs through intense collaboration within (and outside of) the PEC WG**

Research Activity *(Approach)*

- **Overarching goal: compile experimental information about the electronic and chemical properties of the candidate materials produced within the PEC WG**
  - **Determine *status-quo* (includes: find unexpected findings)**
  - **Propose modifications (composition, process, …) to partners**
  - **Monitor impact of implemented modifications**
- **Use a world-wide unique "tool chest" of experimental techniques**
- **Address all technical barriers related to electronic and chemical properties of the various candidate materials, in particular:**
  - **Bulk and surface band gaps**
  - **Energy-level alignment**
  - **Chemical stability**
  - **Impact of alloying/doping**

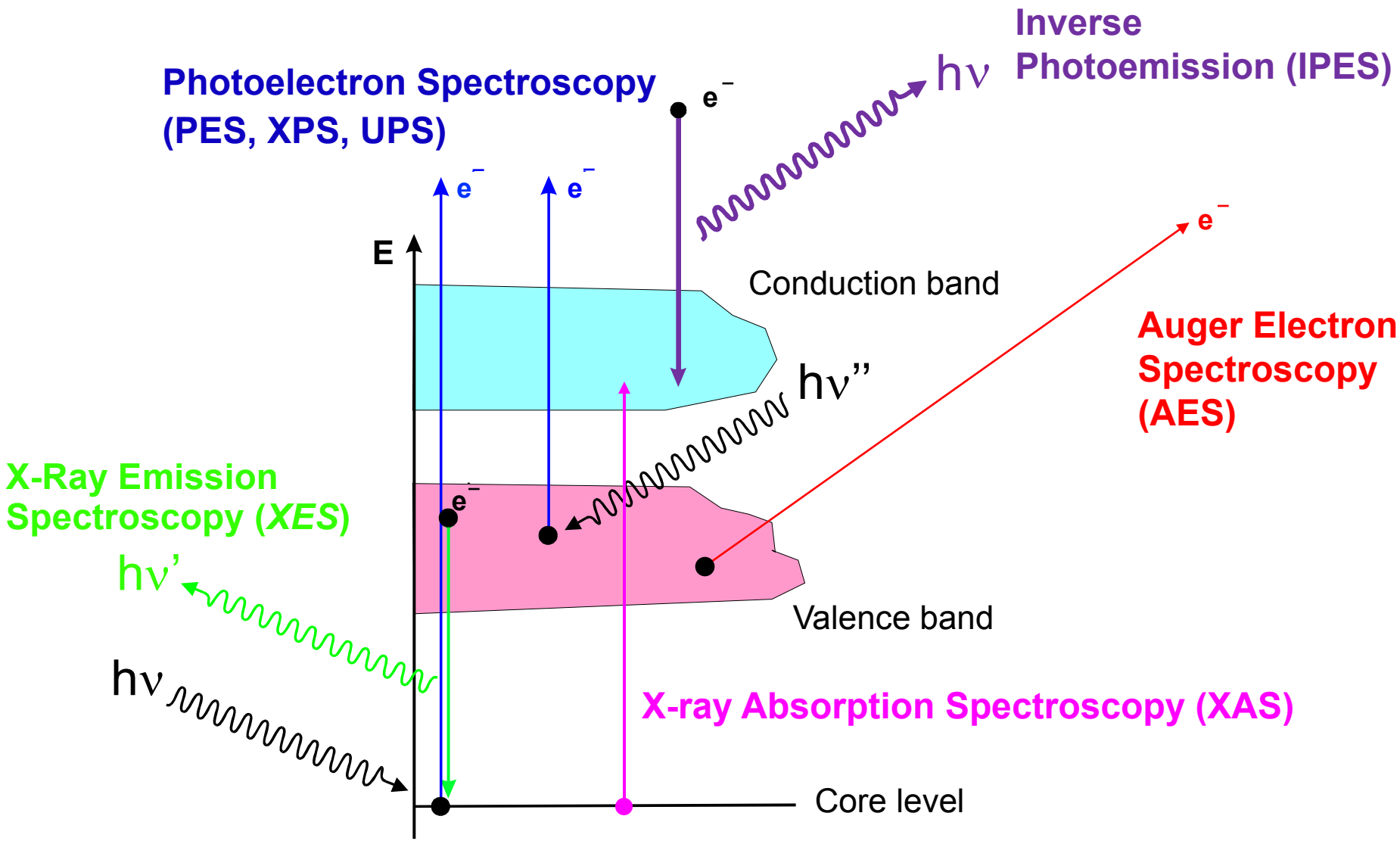
Collaborations

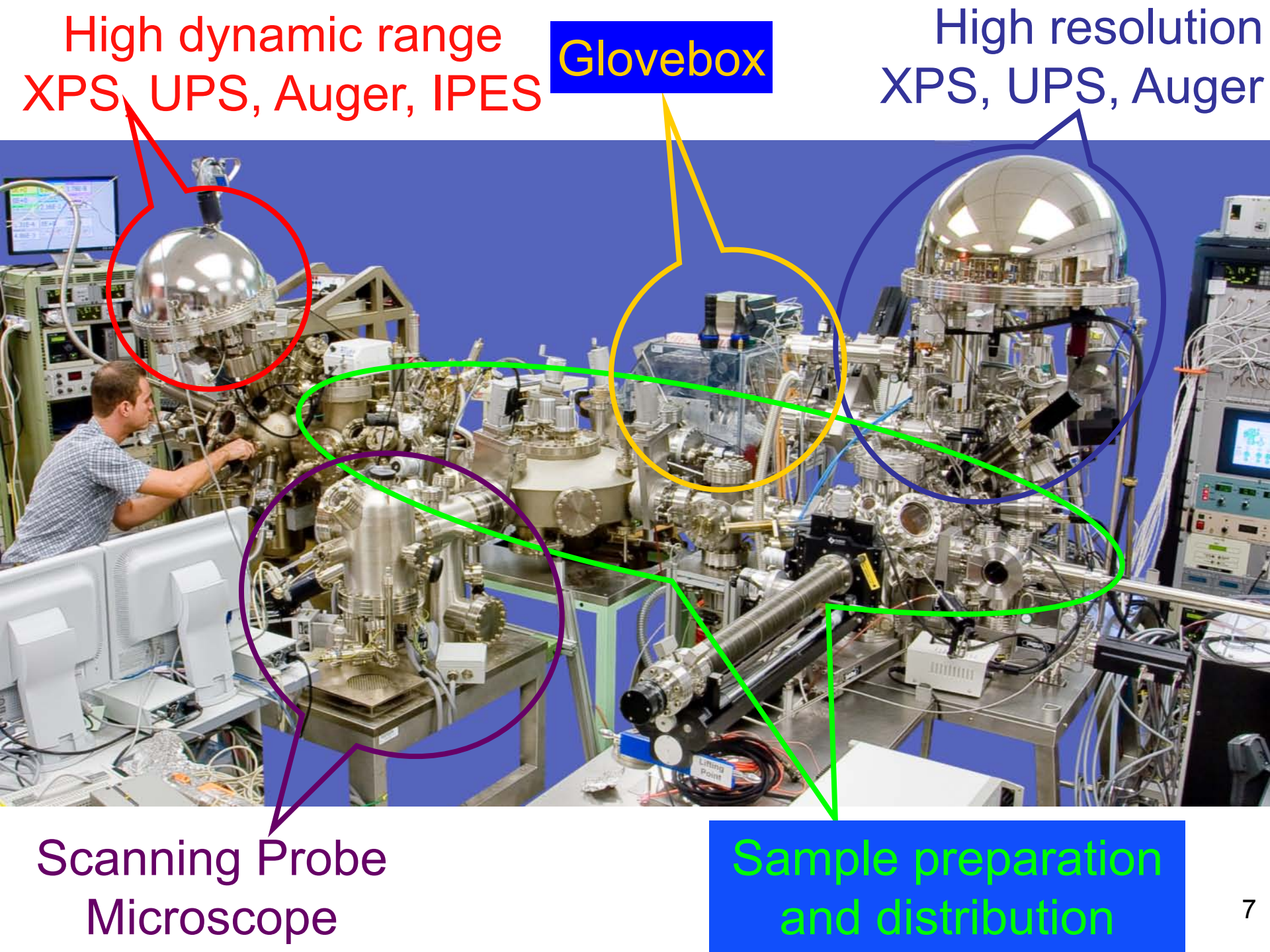
(Relevance, Approach, & Collaborations)

- **Collaborations are at the heart of our activities:**
  - **Supply of samples**
  - **Most important: supply of open questions, issues, challenges**
  - **Interactive interpretation of results**
  - **Joint discussion of potential modifications**
  - **Involvement in implementing modifications**

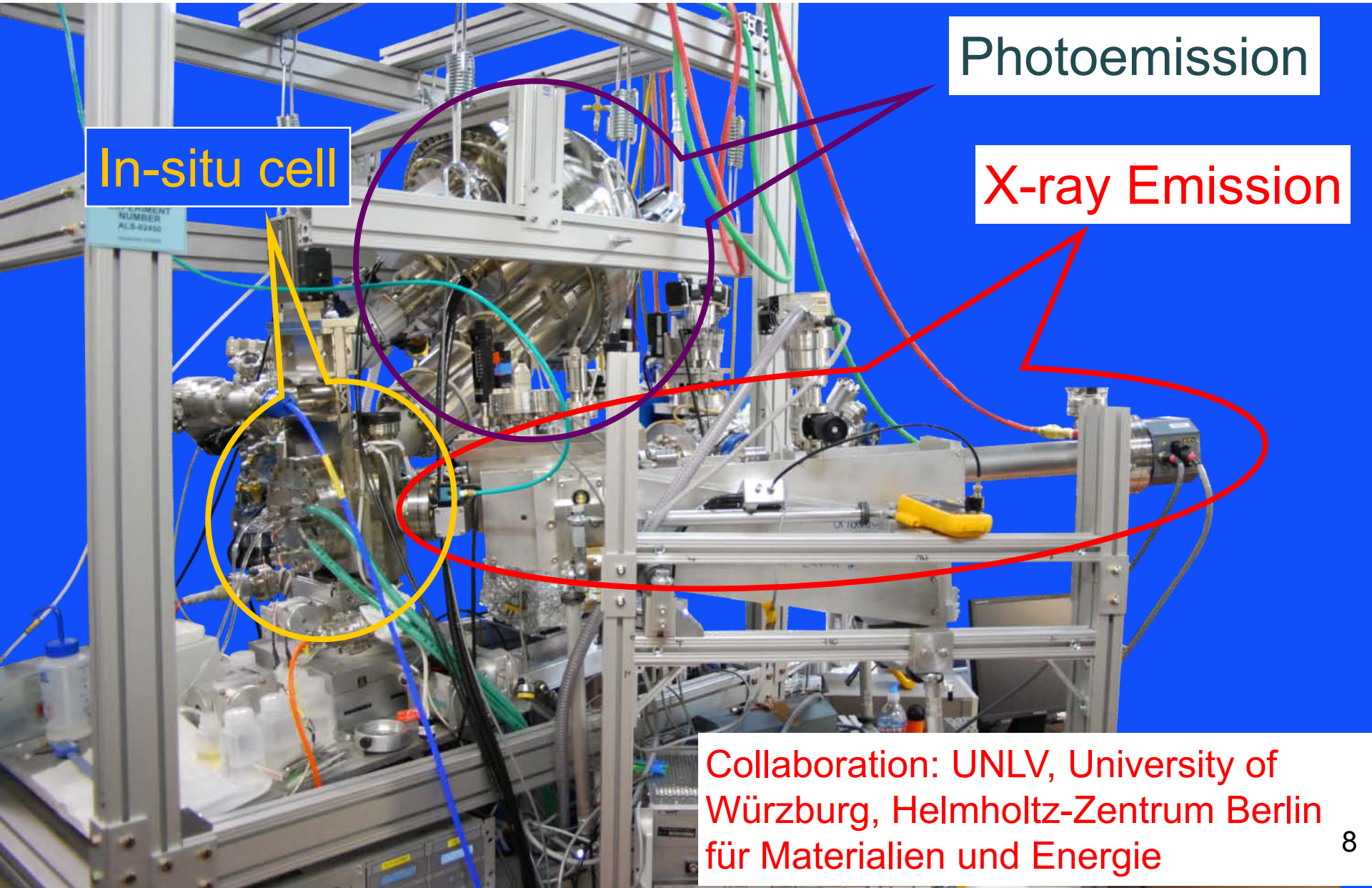
- **Great collaboration partners in the PEC WG:**
  - **U Hawaii (E. Miller et al.): WO_3, $W(X)O(Y)_3$, $Cu(In,Ga)(S,Se)_2$**
  - **NREL (M. Al-Jassim et al., J. Turner et al.): Zn(O,N),** III-V-SC
  - **UC Santa Barbara (E. McFarland et al.): Fe_2O_3 et al.**
  - **MVSystems (A. Madan et al.): SiC**
  - **Stanford U (T. Jaramillo et al.):** WS_2, MoS_2
  - **LLNL (T. Ogitsu et al.):** Theory
  - Open for more!

UV/Soft X-ray Spectroscopies *(Approach)*




High dynamic range
XPS, UPS, Auger, IPES
Glovebox
High resolution
XPS, UPS, Auger
Scanning Probe
Microscope
Sample preparation
and distribution

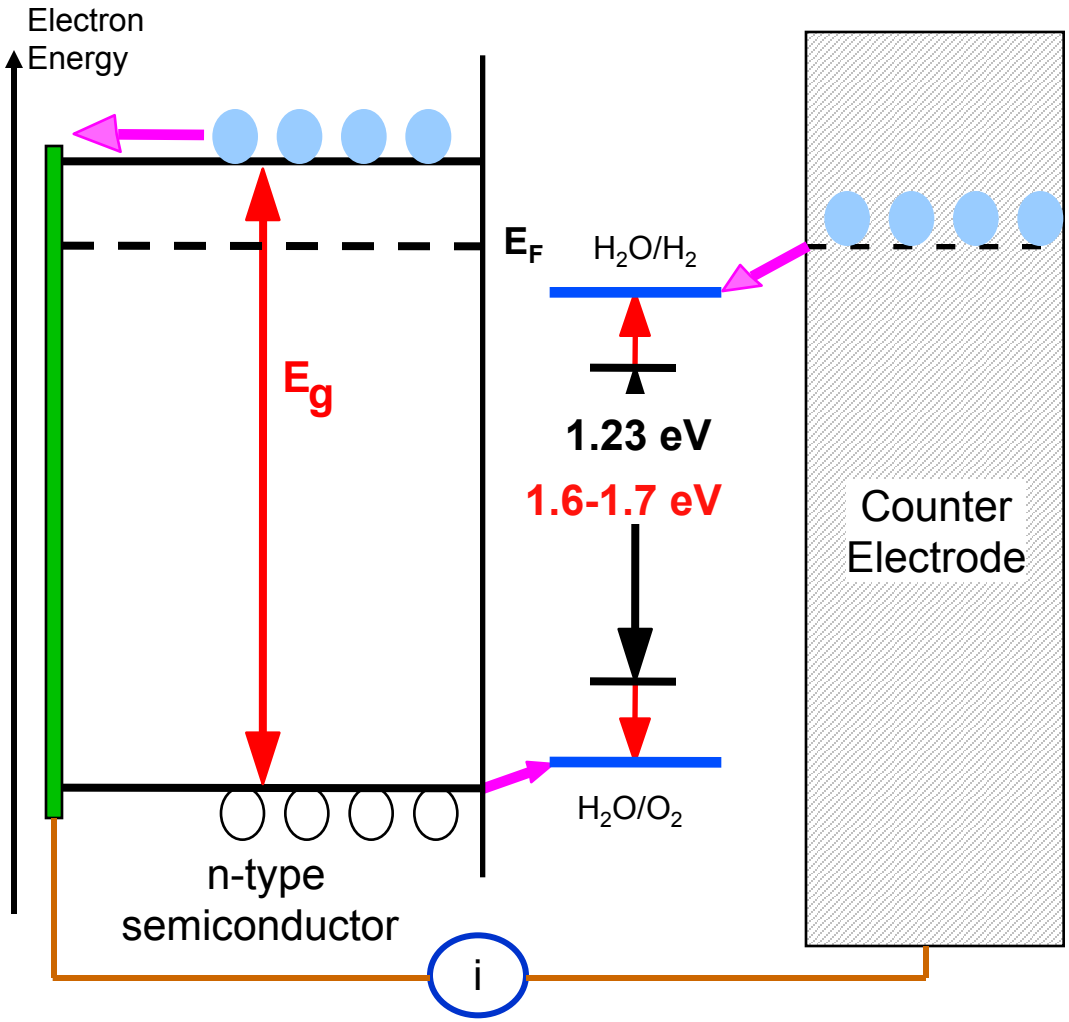
SALSA: Solid And Liquid Spectroscopic Analysis at Beamline 8.0, Advanced Light Source, LBNL



Collaboration: UNLV, University of Würzburg, Helmholtz-Zentrum Berlin für Materialien und Energie

Technical Challenges (the big three)

Material Characteristics for Photoelectrochemical Water Splitting



- **Efficiency –** the bulk band gap (E_g) must be at least 1.6-1.7 eV, but not over 2.2 eV
- **Material Durability –** semiconductor must be stable in aqueous solution
- **Energetics –** the surface/interface band edges must be optimized with respect to the H_2O redox potentials

All must be satisfied simultaneously

After John Turner, NREL

Requirements for PEC Materials

(Relevance)

- Chemical stability
- Optimized bulk band gap for photon absorption
- Optimized band edge positions at the relevant surfaces
- ... (e.g., cost!)

Impact of Mo alloying on WO_3 thin films studied by soft x-ray spectroscopy

With:

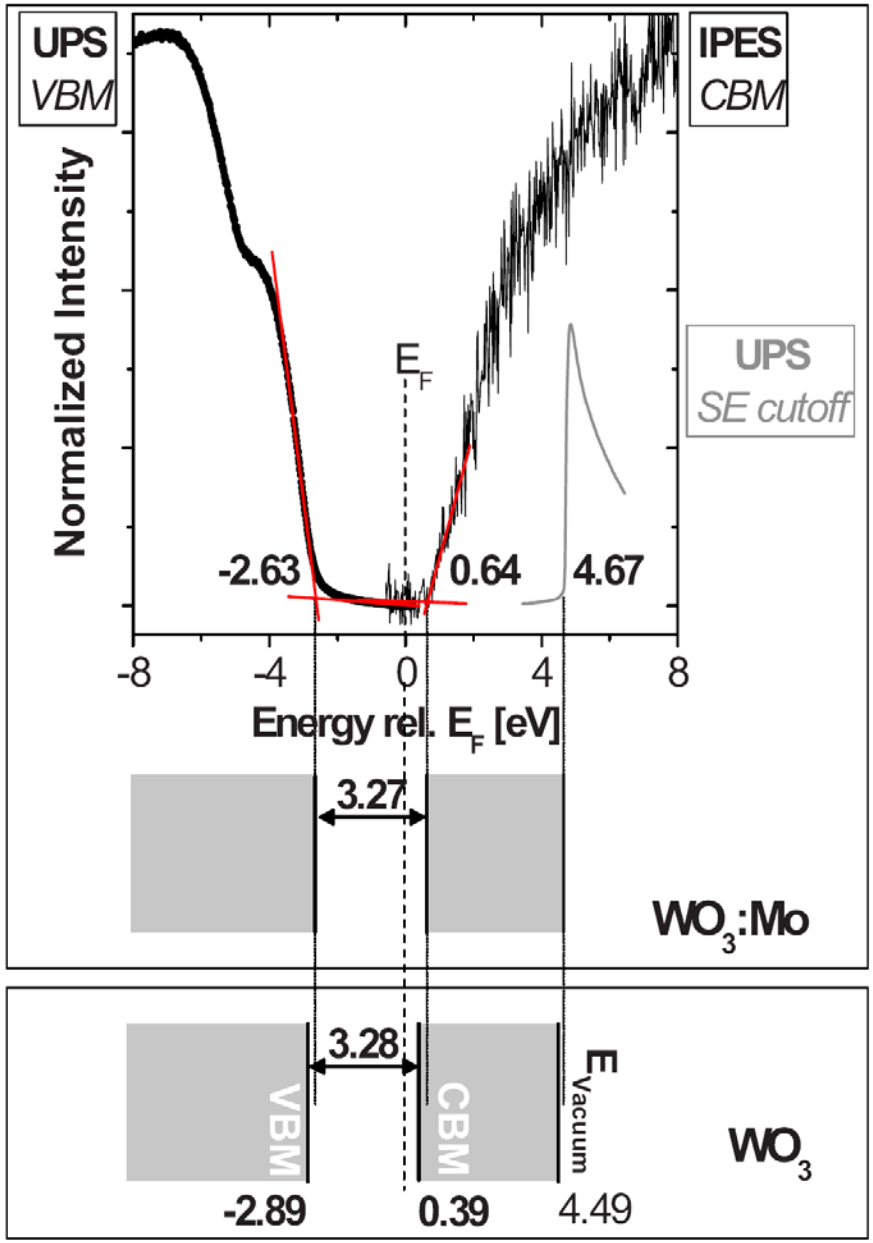
Nicolas Gaillard and Eric Miller

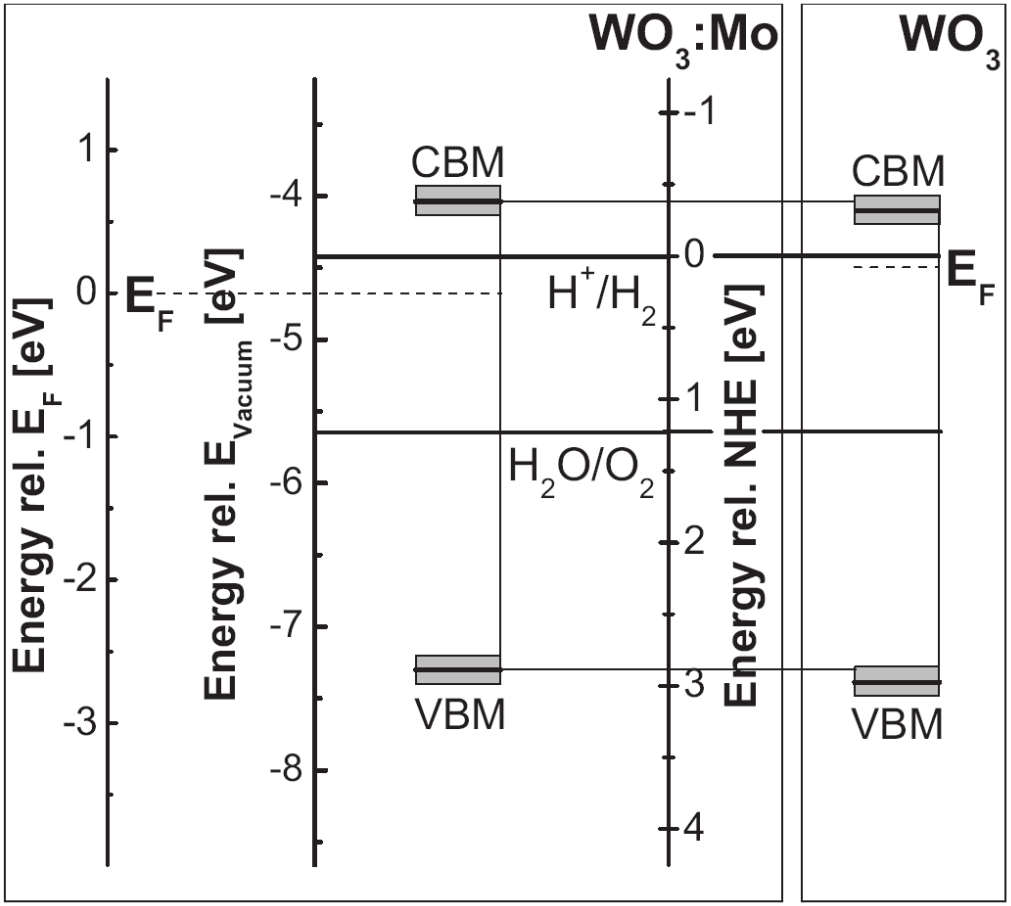
Hawaii Natural Energy Institute, School for Ocean, Earth Science, Technology,
University of Hawaii, Manoa, HI

For more details, please also see PD032 and PD054

Comparison: WO_3 and WO_3:Mo

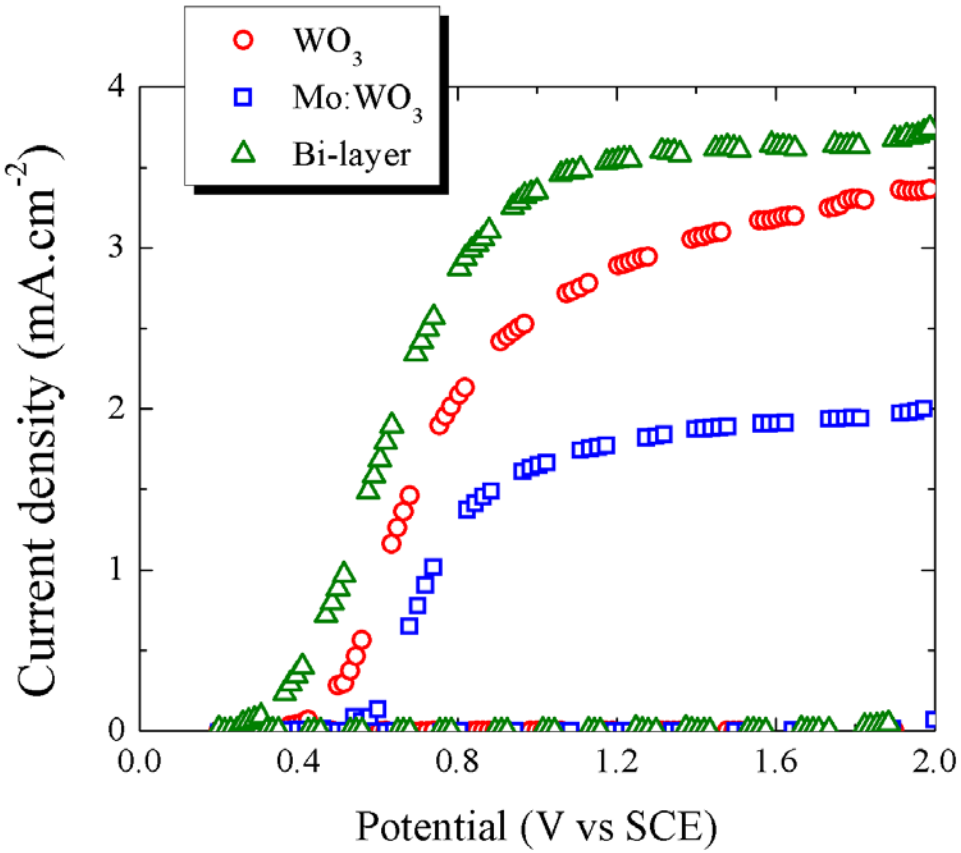
(Accomplishments)

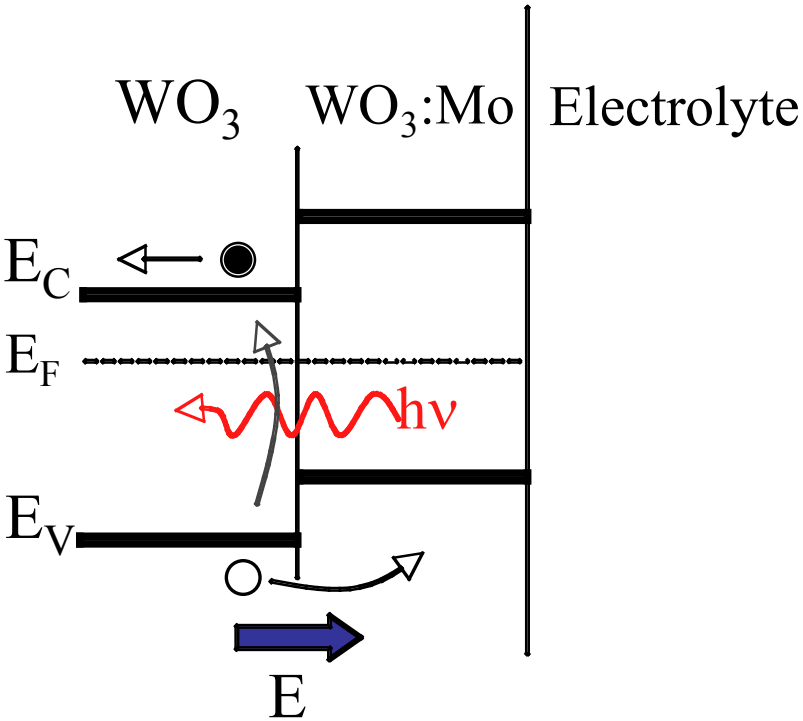




APL **96**, 032107 (2010)

Comparison: WO_3, WO_3:Mo, and WO_3:Mo (300 nm) / WO_3 (2 μm) bilayer





Current-potential characteristics in 0.33 M H_3PO_4 under chopped simulated AM1.5G illumination (scan rate: 25 ms/V)

JMR **25**, 45 (2010)

Impact of PEC testing on a-SiC thin films from the viewpoint of soft x-ray spectroscopy

With:

Feng Zhu, Jian Hu, and Arun Madan

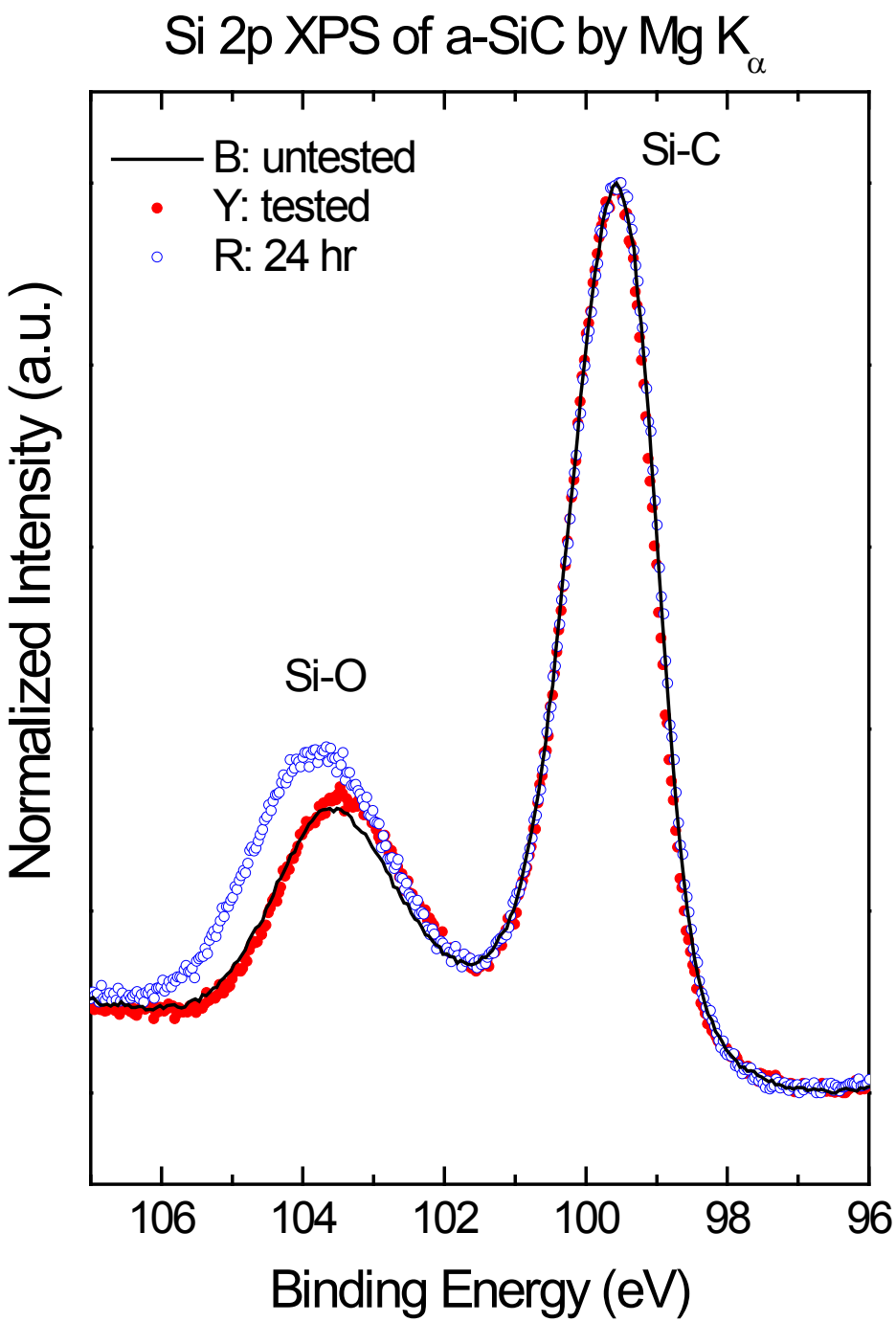
MVSystems, Inc.

Todd Deutsch and John Turner

National Renewable Energy Laboratory, Golden, CO

For more details, please see PD032, PD035, and PD053

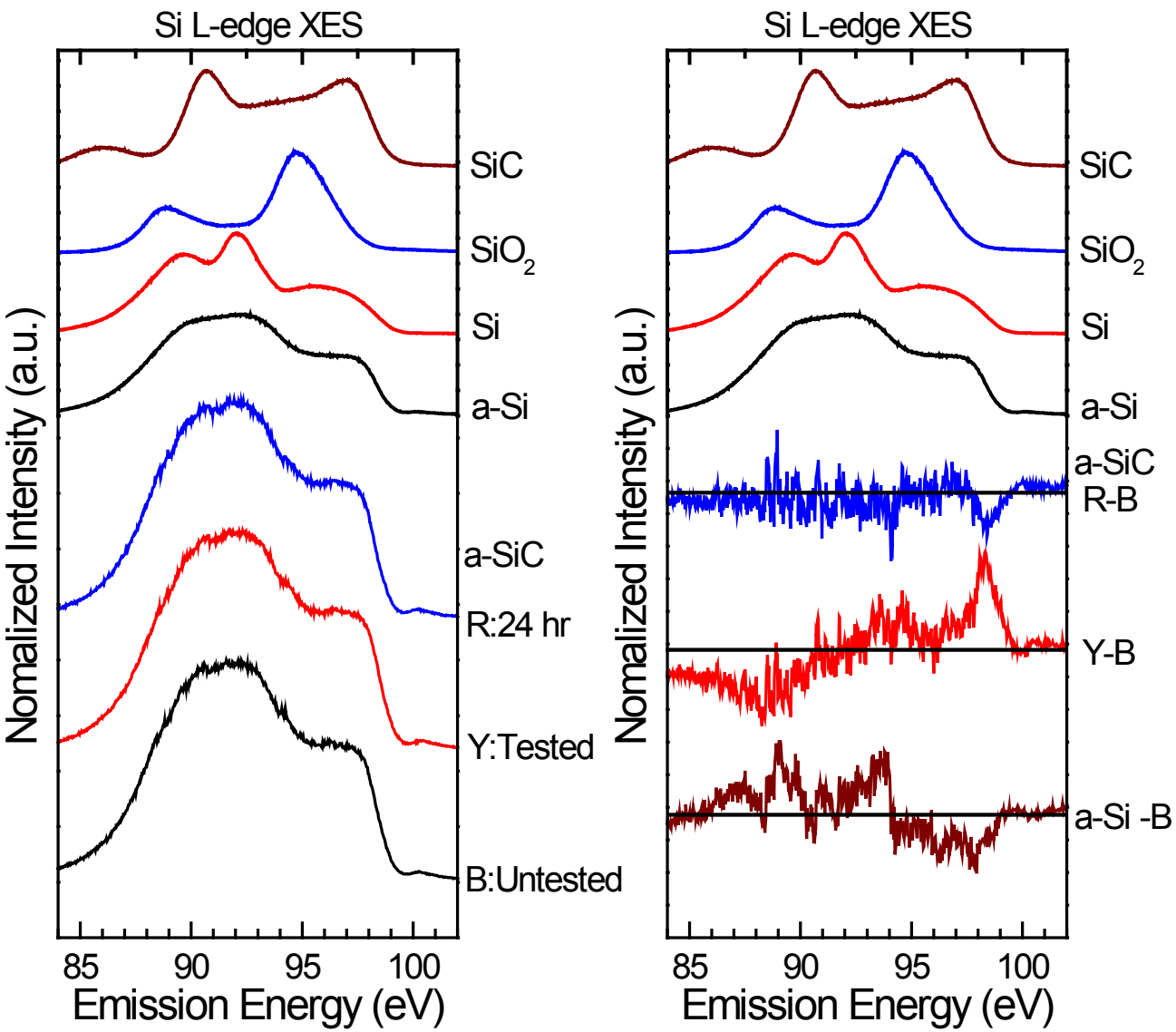
Impact of PEC testing on a-SiC (Accomplishments)



- a-SiC samples:
  - B: untested
  - Y: 2E Chopped light, pH2 PO_4 buffer, -2V vs Ref to 0.05V vs Open Circuit, AM 1.5, Chop at 100 mV increments
  - R: Performed chopped light only at AM 1.5, then 24 hr galvanostatic @ zero applied current under AM 1.5, pH2 PO_4 buffer
- After extended exposure to the electrolyte (sample R), Si-O/Si-C ratio increases, and the center of the Si-O feature shifts toward higher binding energy (closer to that of SiO_2)

Impact of PEC testing on a-SiC

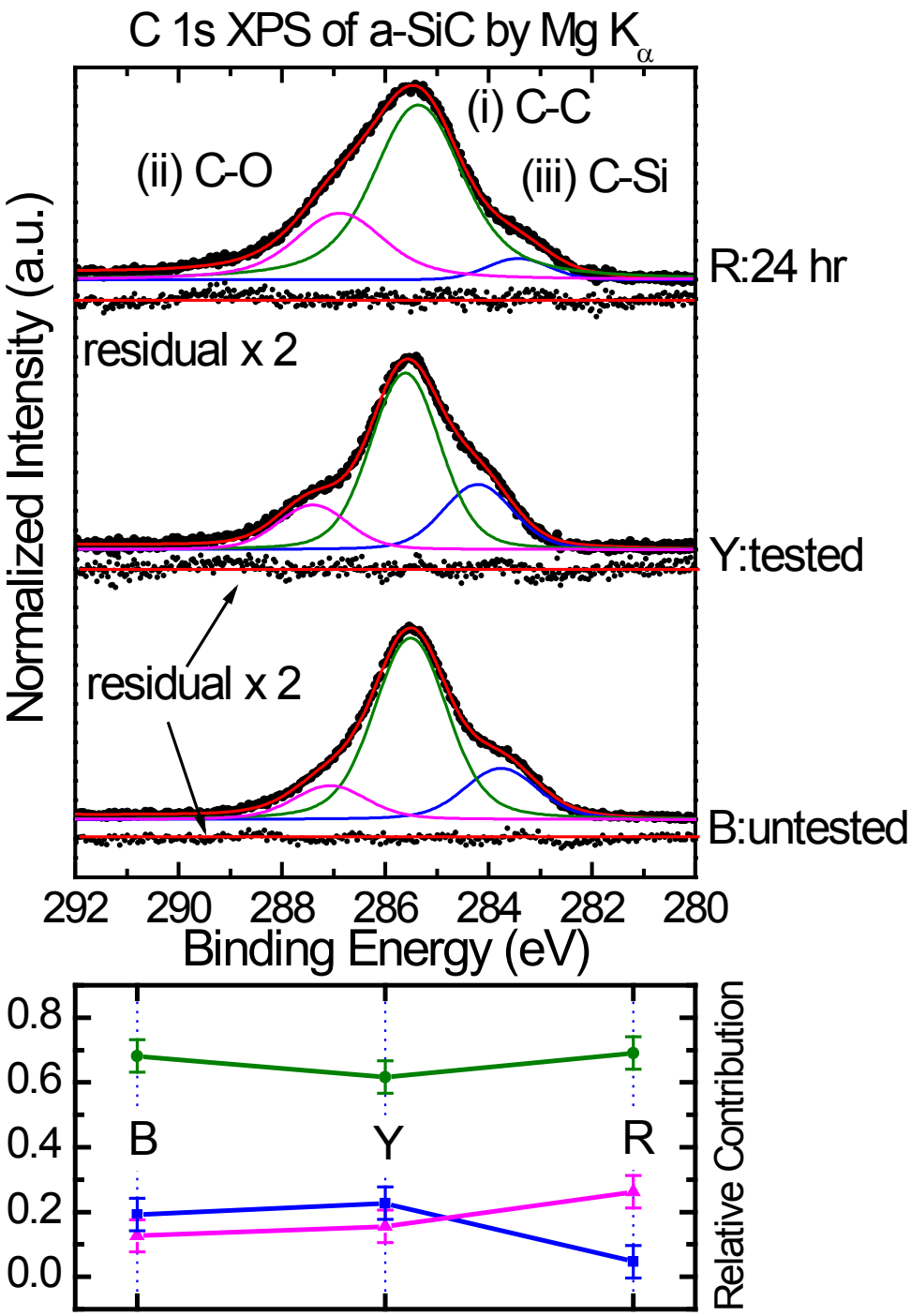
(Accomplishments)



- Si 3d occupied PDOS of a-SiC samples is closer to that of a-Si than other Si references
- Spectral weight near Fermi edge increases after PEC test (sample Y), but decreases after extended exposure to the electrolyte (sample R)

Impact of PEC testing on a-SiC

(Accomplishments)



- All curves were fitted by three Voigt functions and one linear background
- C-O contribution is doubled after extended exposure to the electrolyte (sample R)
- C-Si contribution diminishes greatly after extended exposure to the electrolyte (sample R)

a-SiC Summary

- Extended exposure of a-SiC to acidic electrolyte greatly increases of oxygen–related contents (both C-O and Si-O) and decreases C-Si bonds on the sample surface
- Spectral weight near Fermi energy increases after PEC test, and decreases after extended exposure to the electrolyte - indications of change of chemical environment and valence band maximum (relevant for redox-reactions) at the surface

Investigation of the impact of PEC testing on $CuGaSe_2$ thin films

With:

Jess Kaneshiro, Nicolas Gaillard, and Eric Miller

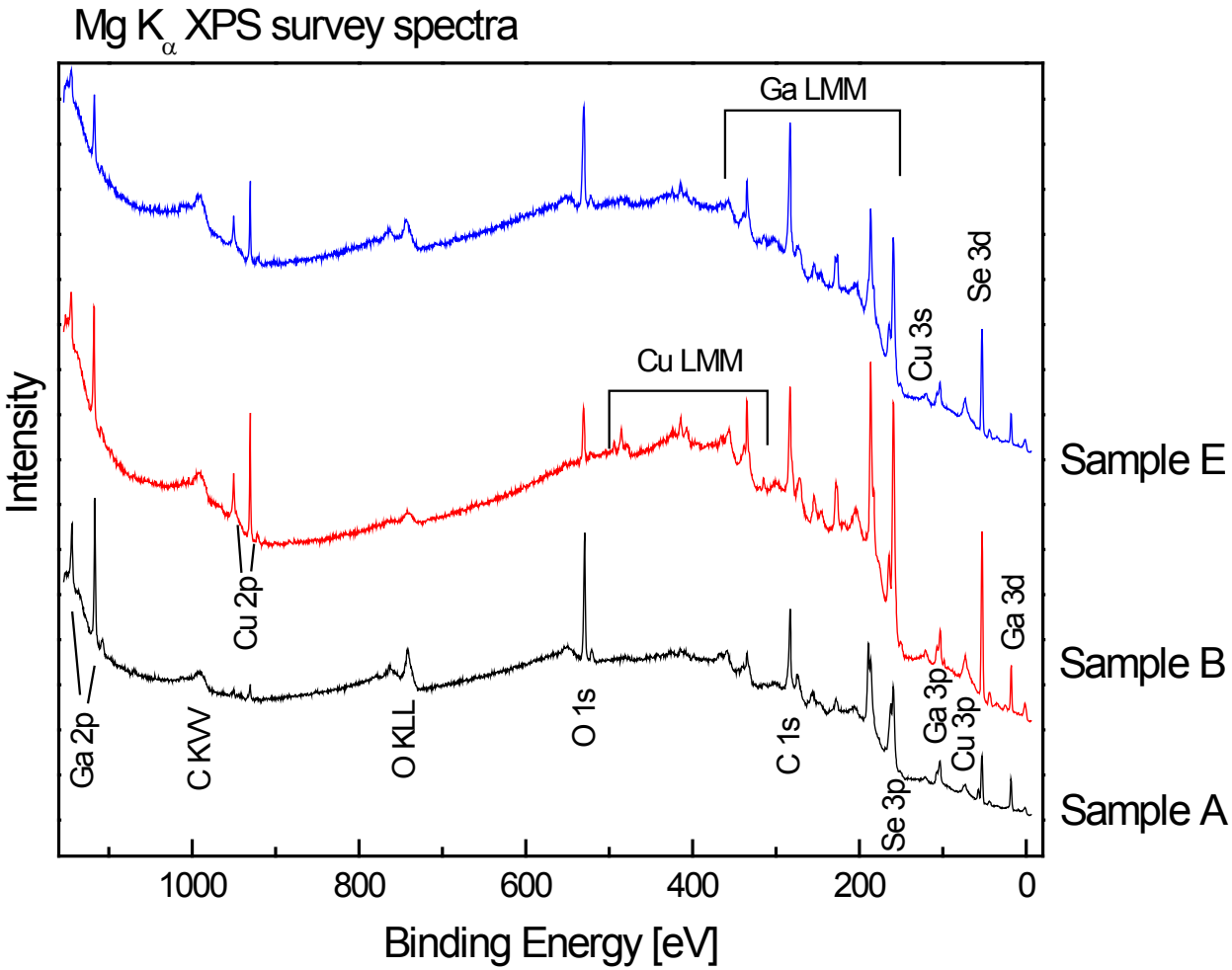
Hawaii Natural Energy Institute, School for Ocean, Earth Science, Technology,
University of Hawaii, Manoa, HI

Todd Deutsch and John Turner

National Renewable Energy Laboratory, Golden, CO

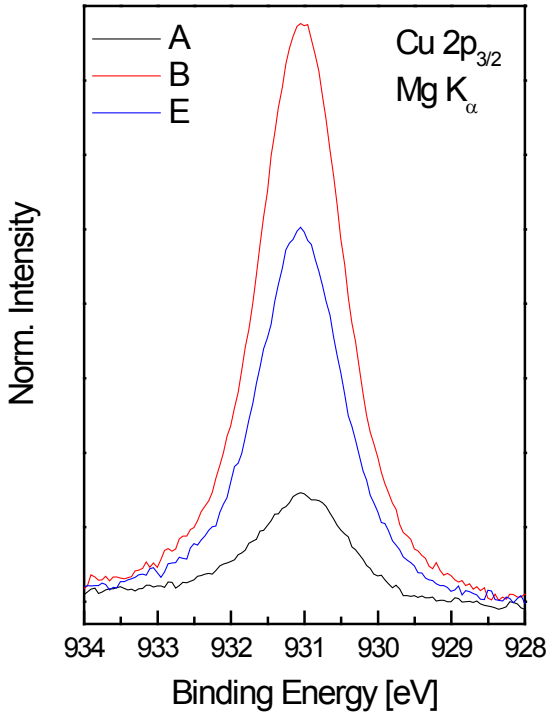
For more details, please see PD032, PD035, and PD055

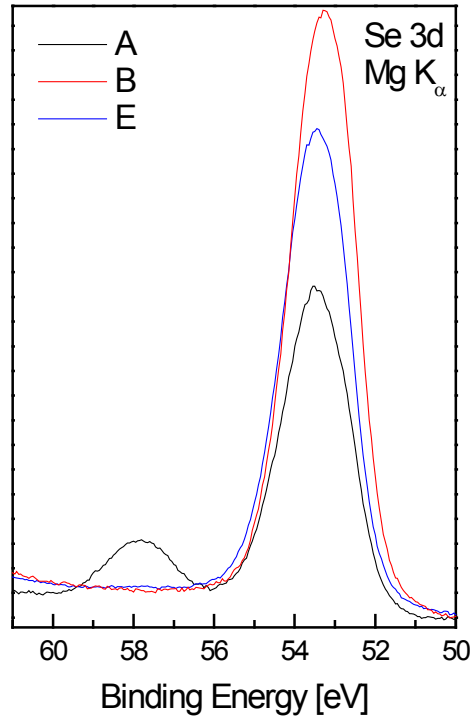
$CuGaSe_2$ thin film surfaces before and after acid exposure and PEC testing *(Accomplishments)*



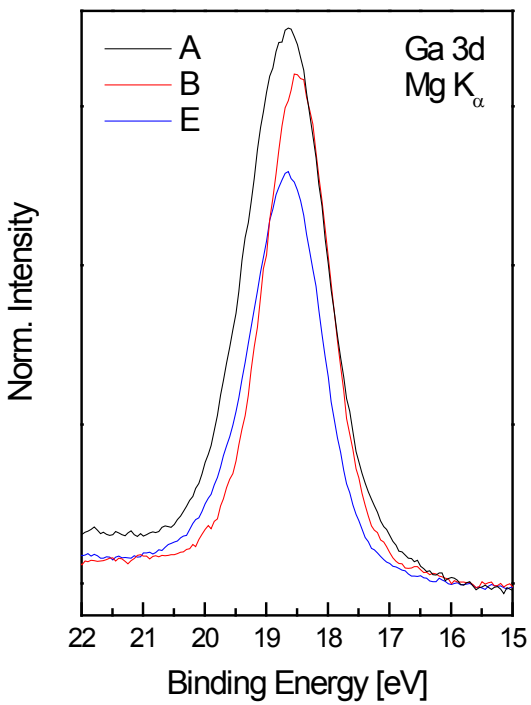
Samples
- A: Untested, control
- B: In 0.5M H_2SO_4 for 24 hr, dark
- E: Illuminated open circuit potential, 2 electrode (sweep - 2.5 V to 0.05 V), 3 electrode IV: -1V to 0.05 V

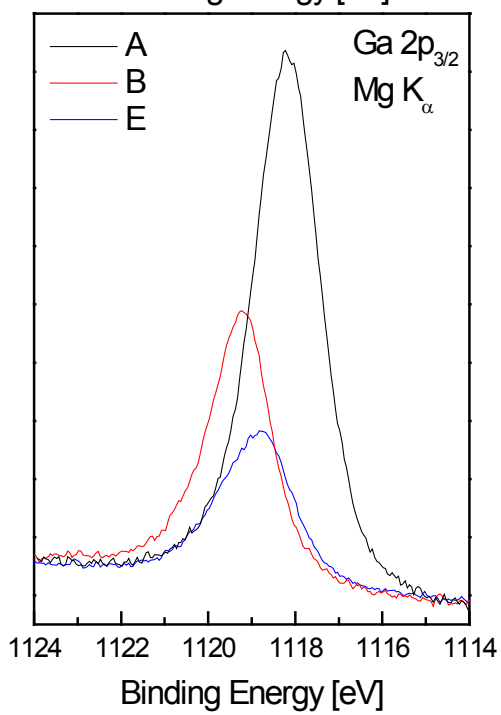
- After exposure to acid (samples B and E), surface content of copper and selenium increases





- Both Cu and Se intensity increases after exposure to acid (sample B) and after PEC testing (sample E) – increase is largest after acid exposure
- SeO_x present at the surface of control sample (15% Se contribution), but is removed when exposed to acid

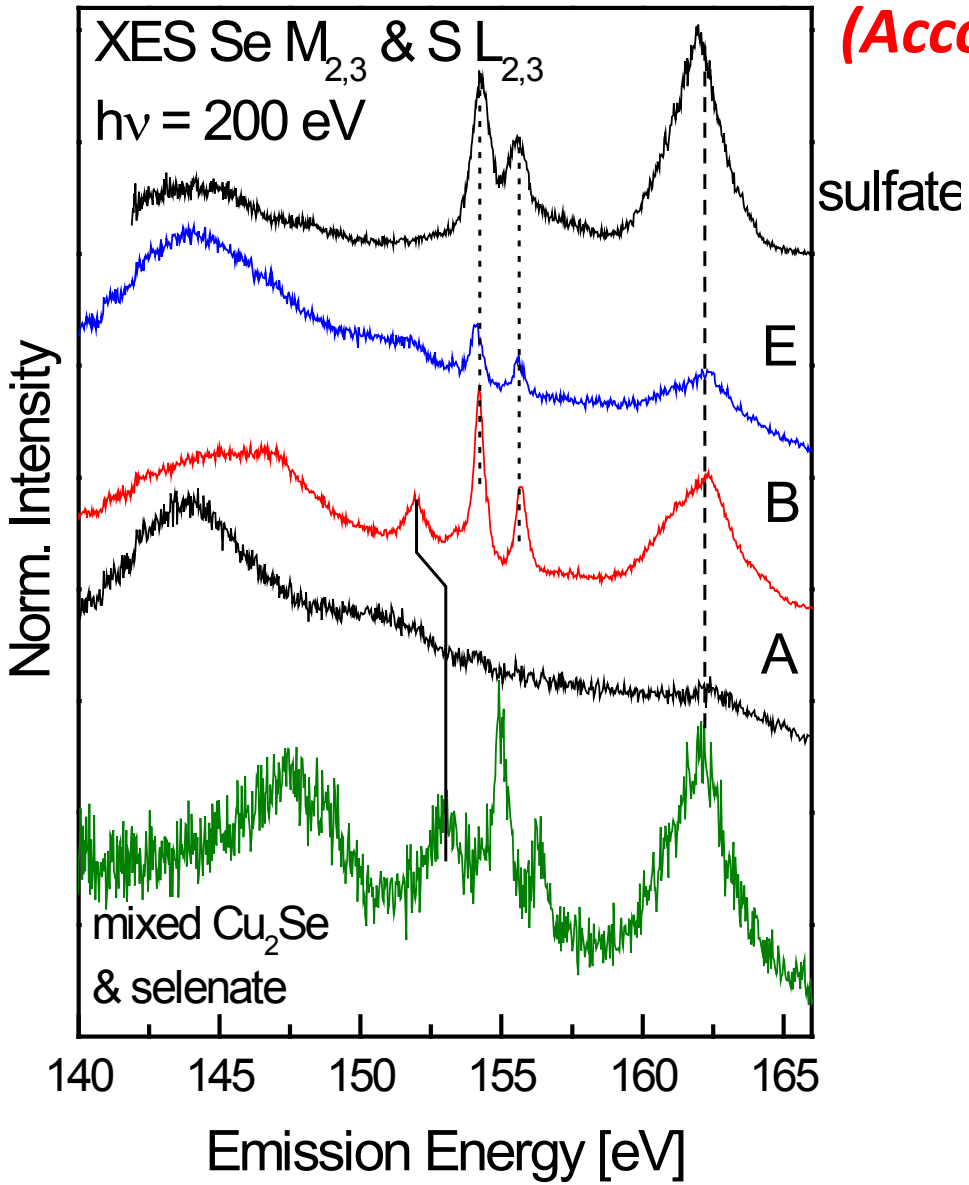




- Unlike Se and Cu, Ga decreases with exposure to acid and testing!
- Ga peak positions shift, indicating significant changes in chemical environment. But directions vary for different core levels (due to valence band nature of Ga 3d?)?

Impact of testing/acid on Se atoms in $CuGaSe_2$

(Accomplishments)



- Untested sample (A) shows Se $M_{2,3}$ emission with weak features at higher energy indicative of oxidized selenium (agree with XPS)
- After being exposed to acid for 24 hr (B), pronounced sulfate and selenate features
- Tested sample (E) has weaker sulfate features and stronger $CuGaSe_2$ Se $M_{2,3}$ emission
- Sample exposure to H_2SO_4 results in sulfate formation/deposition on surface

$CuGaSe_2$ summary

- Exposure to H_2SO_4 changes the composition at $CuGaSe_2$ surface
  - Copper and selenium increase
  - Gallium decrease (dissolution?)
- Reduction of Selenium oxides and sulfate formation as a result of acid exposure

Surface Composition of Fe_2O_3 Thin Films – correlation with PEC performance

With:

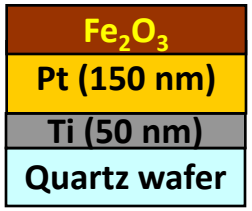
A. Forman, A. Kleiman-Shwarsctein, and Eric McFarland

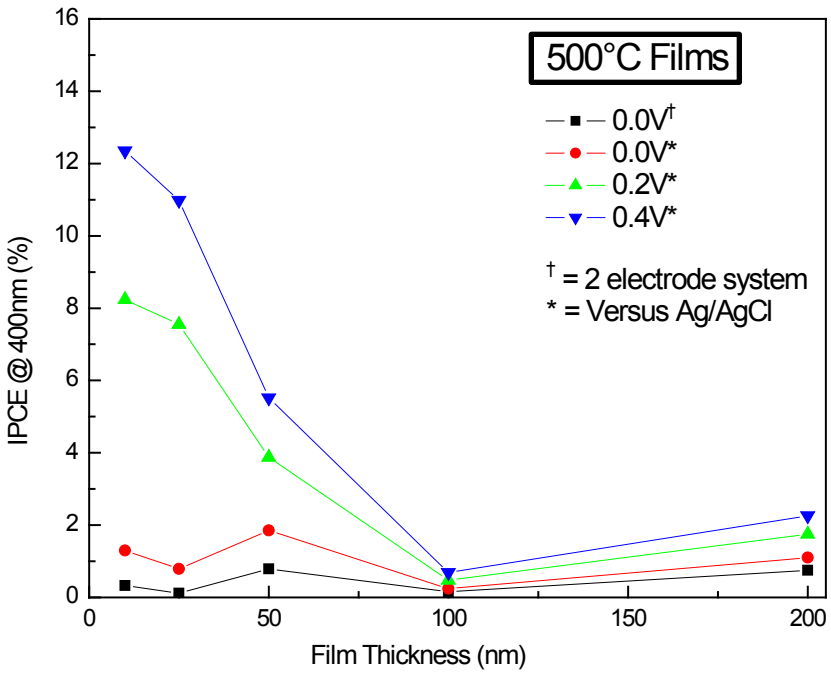
University of California, Santa Barbara

For more details, please see PD032 and PD034

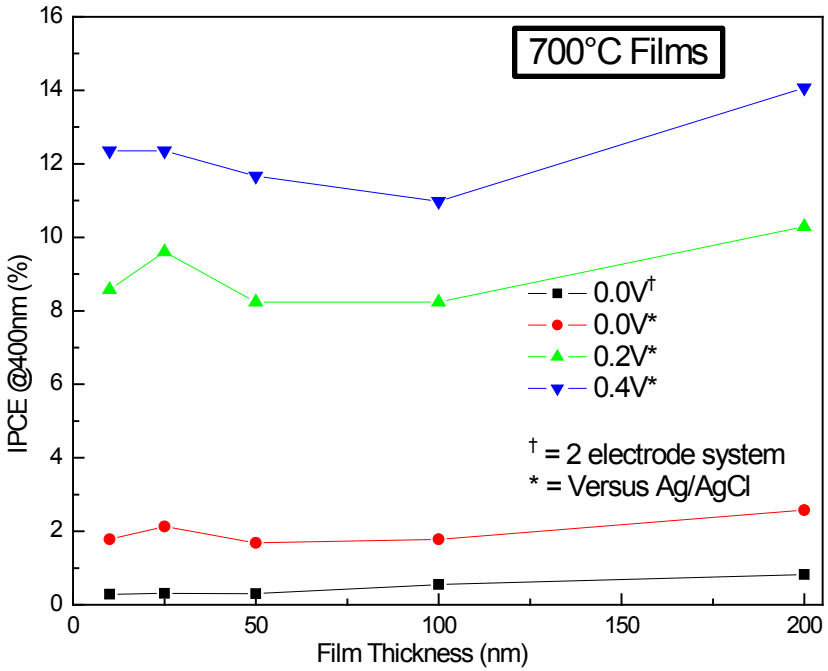
Overview

- UCSB has synthesized Fe_2O_3 thin films as schematically shown on right
- Samples were calcined at for 4 hours at the temperature indicated
- Films calcined at 500°C exhibited a "bathtub" shaped IPCE thickness-dependence not seen in 700°C films





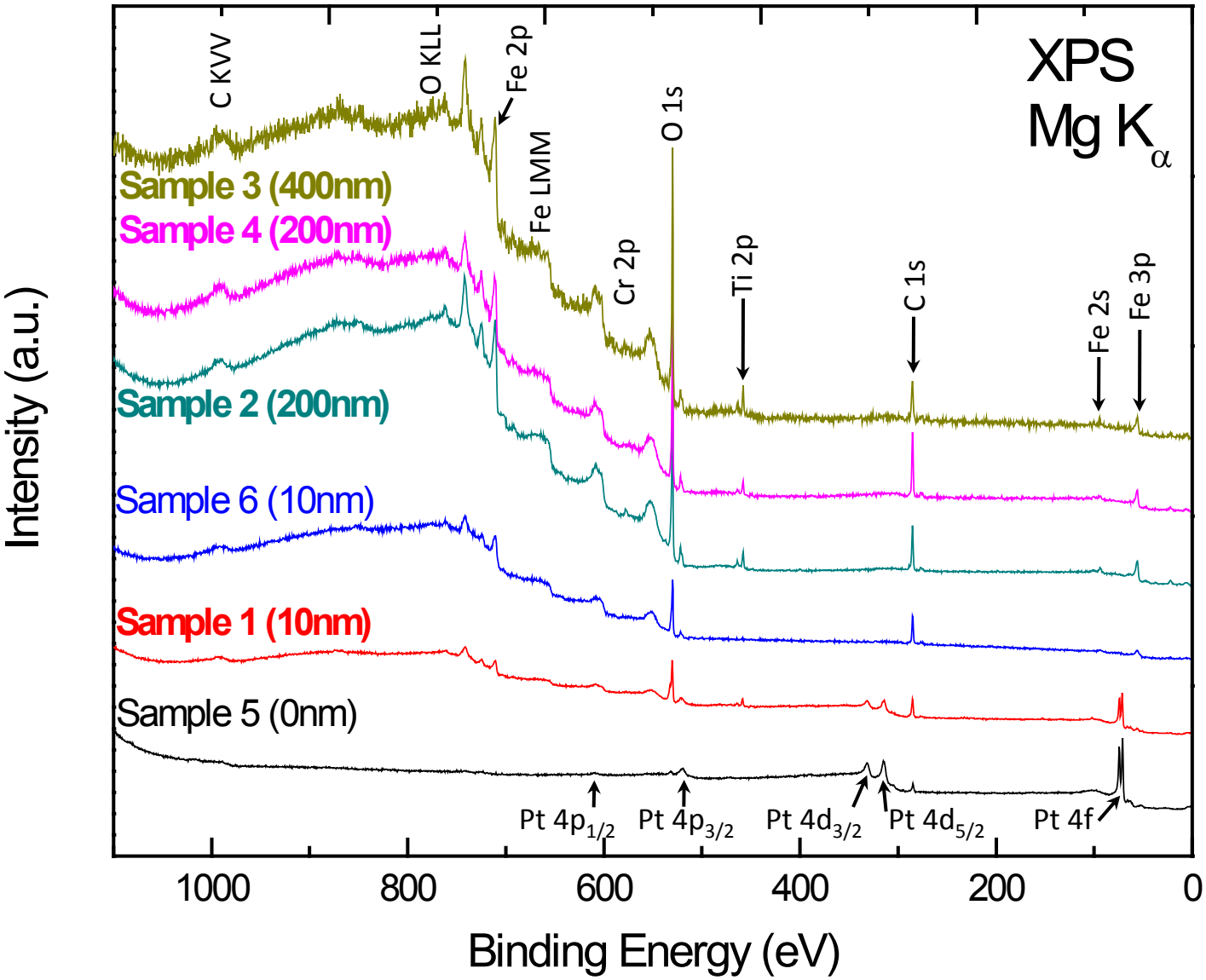
- UCSB initially reported sample thickness dependence (when annealed at 500°C)
- Above 100 nm, performance improves up to 500nm films (not shown)



- Annealing at 700°C appears to stabilize sample

IPCE data from Alan Kleiman and Arnold Forman University of California, Santa Barbara

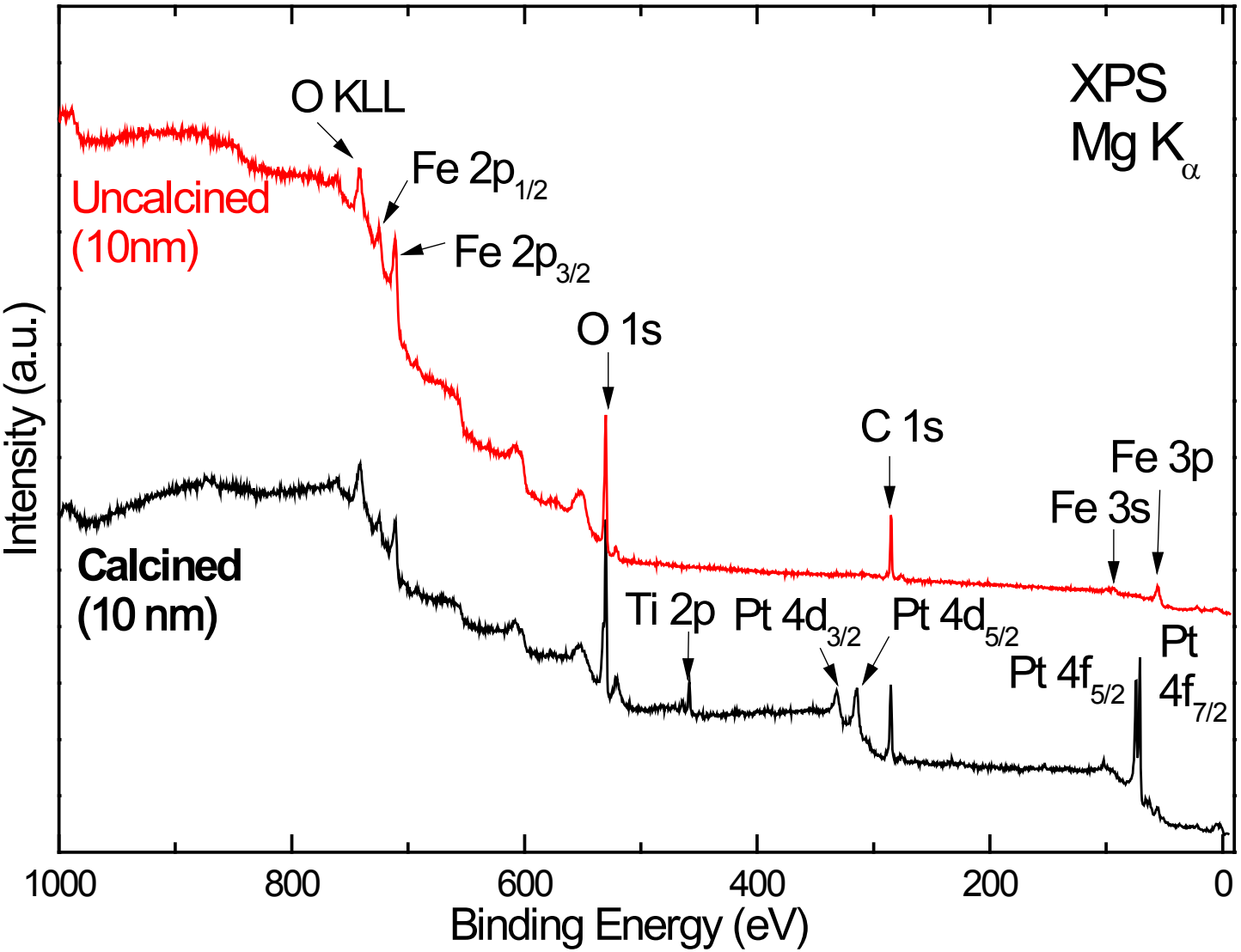
Survey Spectra of Fe_2O_3 films with varying thickness, before and after calcination (Accomplishments)



- Calcined samples (700°C for 4 hours) are represented by bold font (samples 1-4)
- XPS spectra of calcined samples show Ti peaks not present in uncalcined samples

Effect of calcination on thin Fe_2O_3 samples

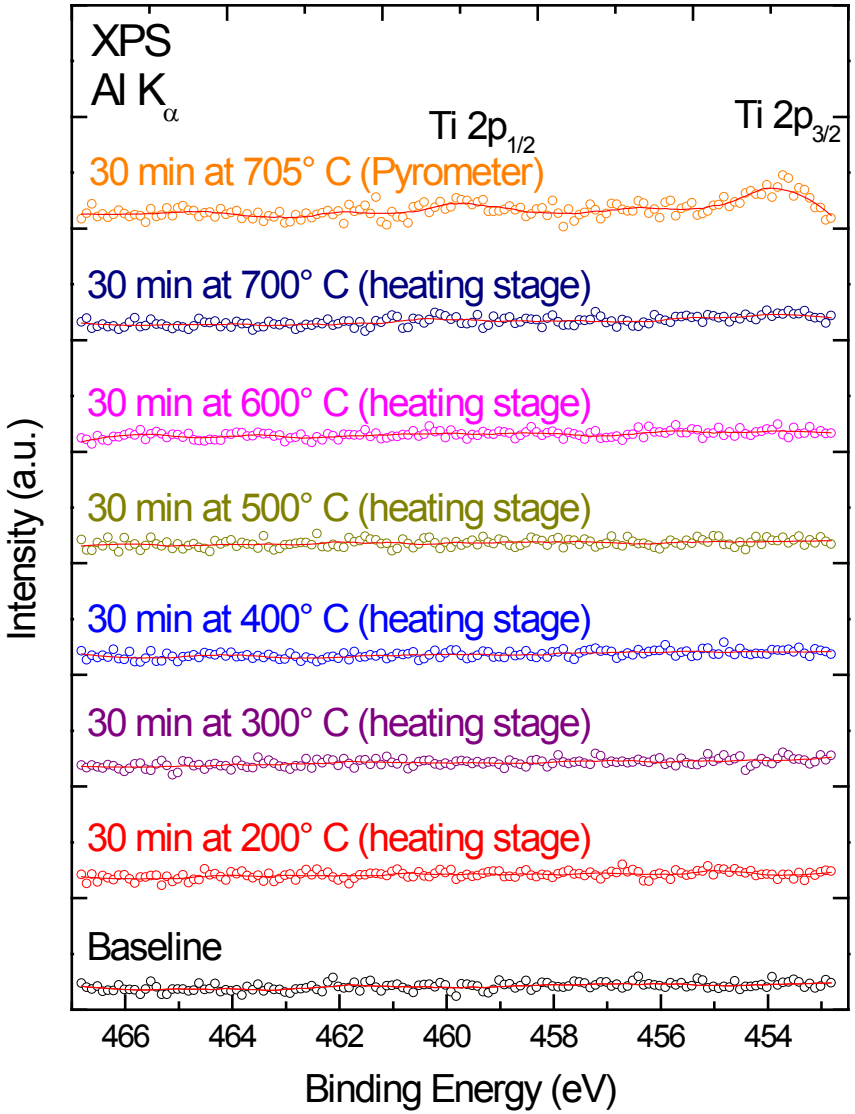
(Accomplishments)

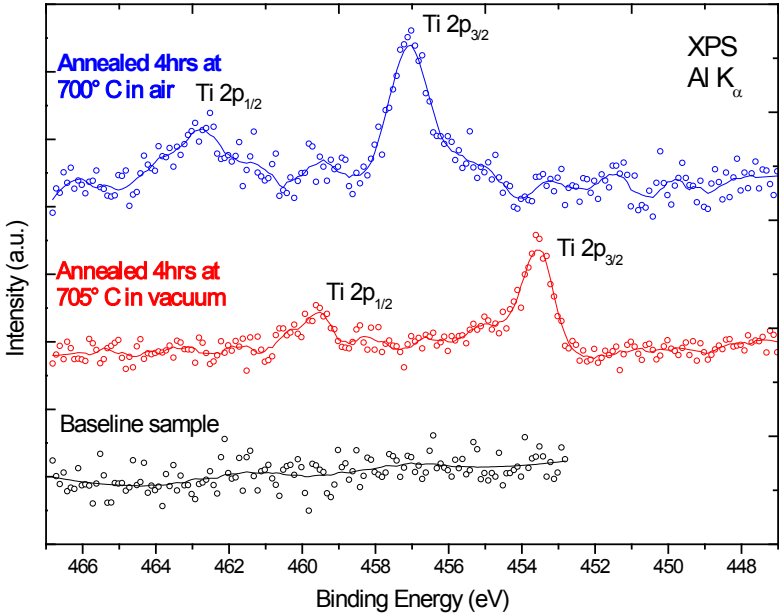


- The 10 nm calcined sample shows Pt peaks not seen in thicker or uncalcined samples

Ti emerges in an annealing series!

(Accomplishments)

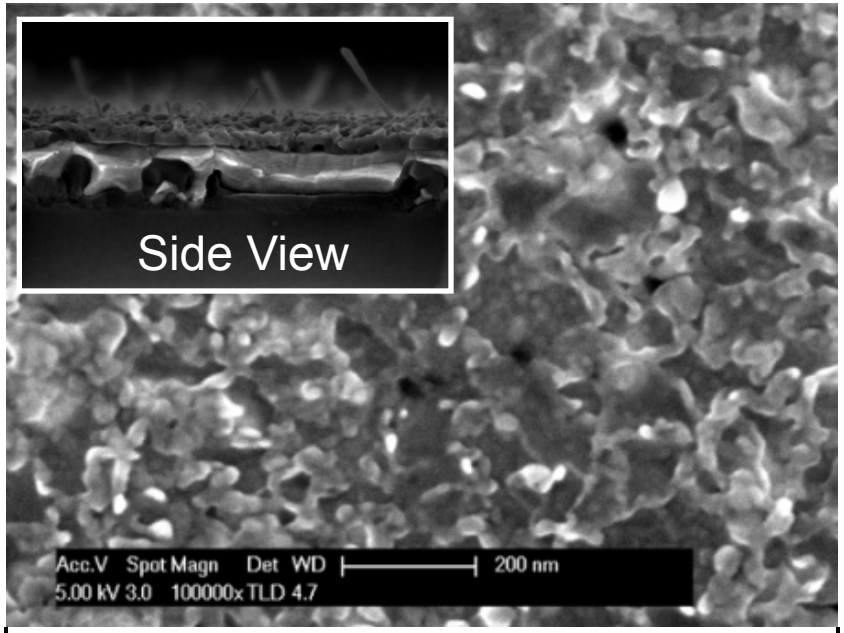




- Annealing series experiments (Pt surface sample/0 nm Fe) show the emergence of Ti between 650°C and 700°C
- TiO_2 seen when annealed in air

SEM Images of Film Surfaces

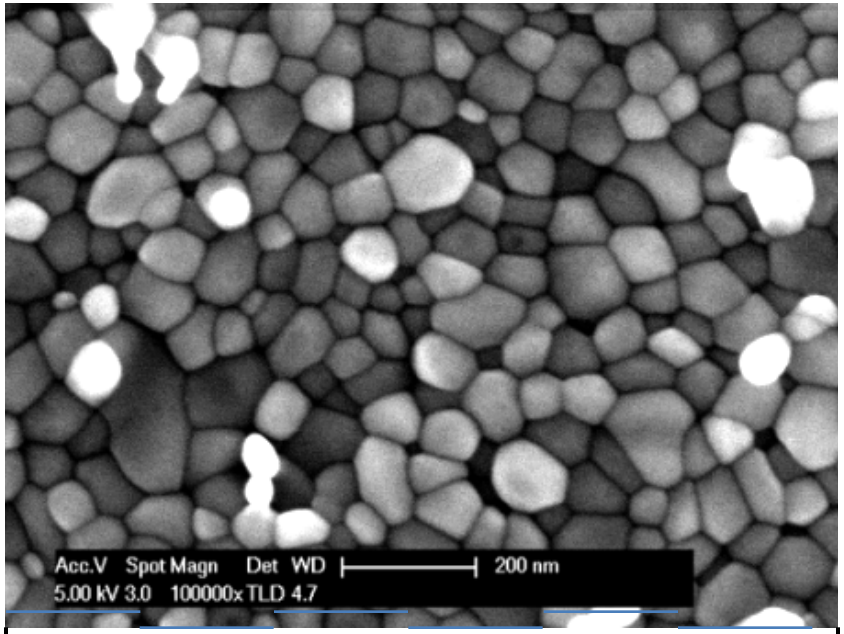
10 nm Calcined Film



1.3μm

Acceleration Voltage: 5.00kV
Magnification: 100,000x

200 nm Calcined Film



1.3μm

Acceleration Voltage: 5.00kV
Magnification: 100,000x

Images courtesy Alan Kleiman and Arnold Forman
University of California, Santa Barbara

- Side view shows needle and island growth on calcined samples
- Islands begin to overlap on thicker films – resulting in more complete coverage

Summary of Fe_2O_3 results

- At a calcination temperature of 700 C, Ti diffusion from the substrate to the Fe_2O_3 surface occurs
- In thin Fe_2O_3 films, Pt signals are observed at the surface
- Ti appears to “stabilize” IPCE performance in samples calcined at 700 C (w.r.t. film thickness)
- Dip in IPCE performance of films calcined at 500 C is speculated to be due to the Pt catalytic response in thin films and increasing photocatalytic response corresponding to increase in Fe_2O_3 (Ti) film thickness

Research Plan & Basis for Continuation of Research

(Proposed Future Work)

- Continue the collaborations with our existing partners and bring new partners "on board"
  - New materials classes: (In,Ga)(P,N) with NREL, WS_2 and MoS_2 with Stanford
  - Correlation with theory from new WG partner (LLNL)
- Determine electronic and chemical properties of various PEC candidate materials (see list on collaboration slide) and answer as many questions as possible
- Study the impact of material modifications by the collaboration partners (e.g., alloying, doping, …)
- Study material durability after exposure to a variety of ambient environments
- Find unexpected things (e.g., guest species)

Summary (Relevance)

- Approach allows unprecedented insight into the electronic and chemical structure of PEC candidate materials from within (and outside of) the DOE WG
- Portfolio of experimental techniques ranging from “standard” to “pushing the edge forward”
- Requires close collaboration with synthesis groups, theory groups, and other characterization groups
- Results will be as good as the questions we ask!

- Addresses materials performance, lifetime, and cost directly or indirectly through collaboration partners