Characterization of Materials for Photoelectrochemical Hydrogen Production (PEC)

Clemens Heske

Department of Chemistry,
University of Nevada, Las Vegas

May 12, 2011

Project ID # PD051

Overview

Timeline

- Project start date: 5/6/08
- Project end date: 9/30/11
- Percent complete: 83%

Barriers

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

Budget

- Total project funding
  - DOE share: $390k
  - Contractor share: $97.5k
- Funding received in FY10: $100k
- Funding for FY11: $90k

Partners

- Interactions/collaborations: DOE EERE PEC WG (NREL, LLNL, HNEI, UCSB, Stanford, MVSystems), 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*)
- **Provide characterization support for surface validation**
- **Address materials performance, materials lifetime, and capital costs through intense collaboration within (and outside of) the PEC WG**

Research Activity (Approach)

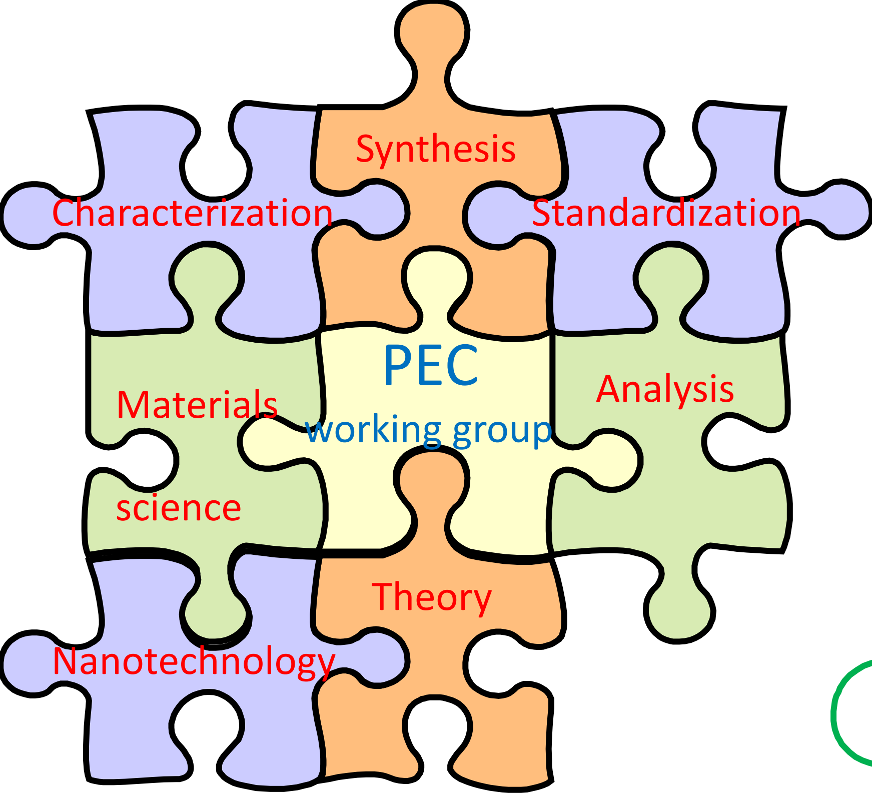
- **Overarching goal: compile experimental information about the electronic and chemical properties of the candidate materials studied within the PEC WG**
  - **Determine *status-quo* (includes: find unexpected findings)**
  - **Propose modifications (composition, process, …) to partners**
  - **Monitor 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)

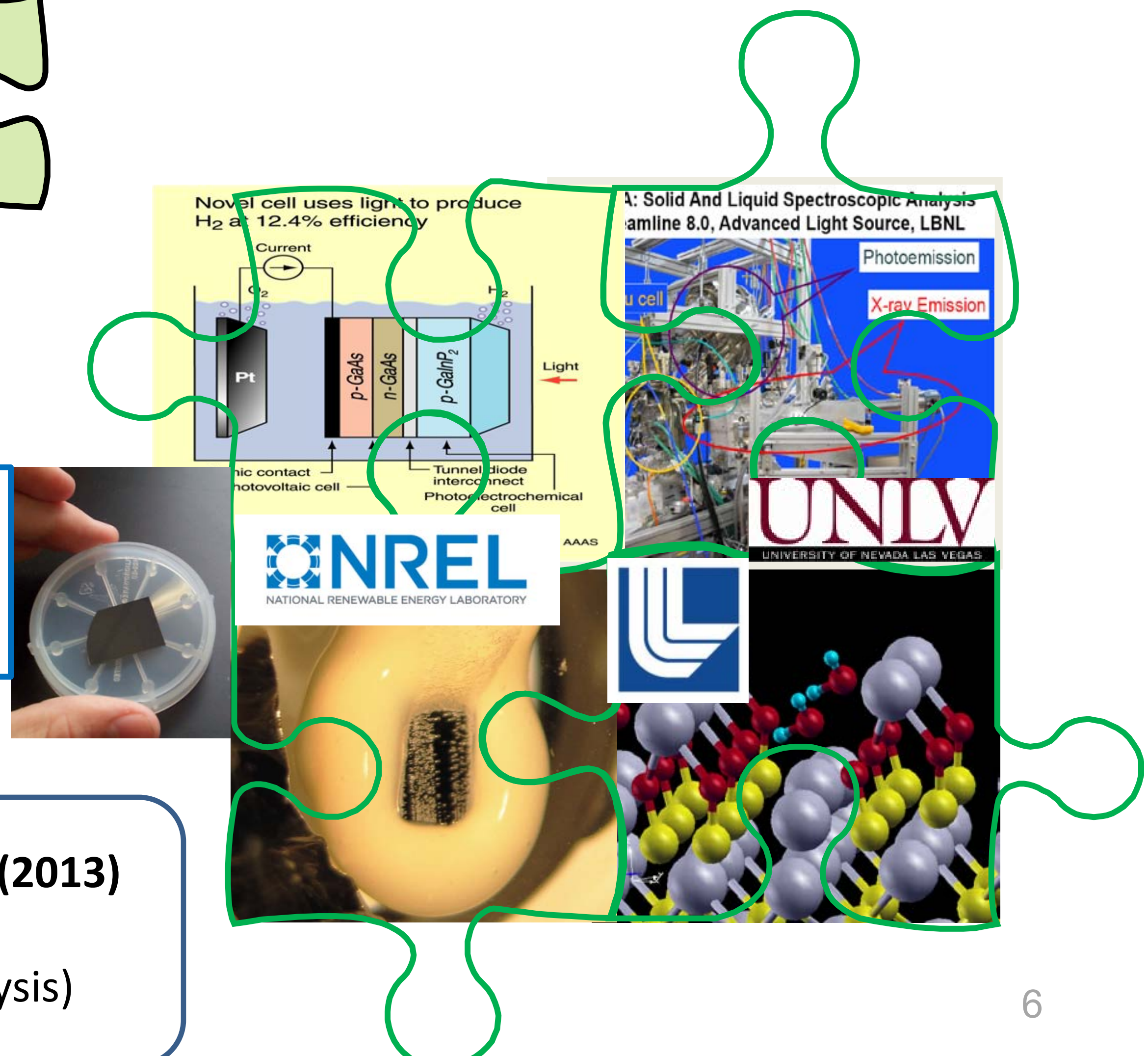
- **Collaborations are at the heart of our activities:**
  - Supply of samples
  - Most important: supply of open questions, issues, challenges
  - Interactive interpretation of results
  - Joint discussion of potential modifications
  - Involvement in implementing modifications

- **Great collaboration partners in the PEC WG:**
  - NREL: $(Ga,In)P_2$
  - UC Santa Barbara: Fe_2O_3 et al.
  - Stanford U: MoS_2
  - LLNL: Theory ($(Ga,In)P_2$, liquid/solid interfaces)
  - U Hawaii/HNEI: WO_3, $W(X)O(Y)_3$, $Cu(In,Ga)(S,Se)_2$



PEC Working Group:

Evaluating working directions
Sharing and building-up knowledge
Accelerating research progress



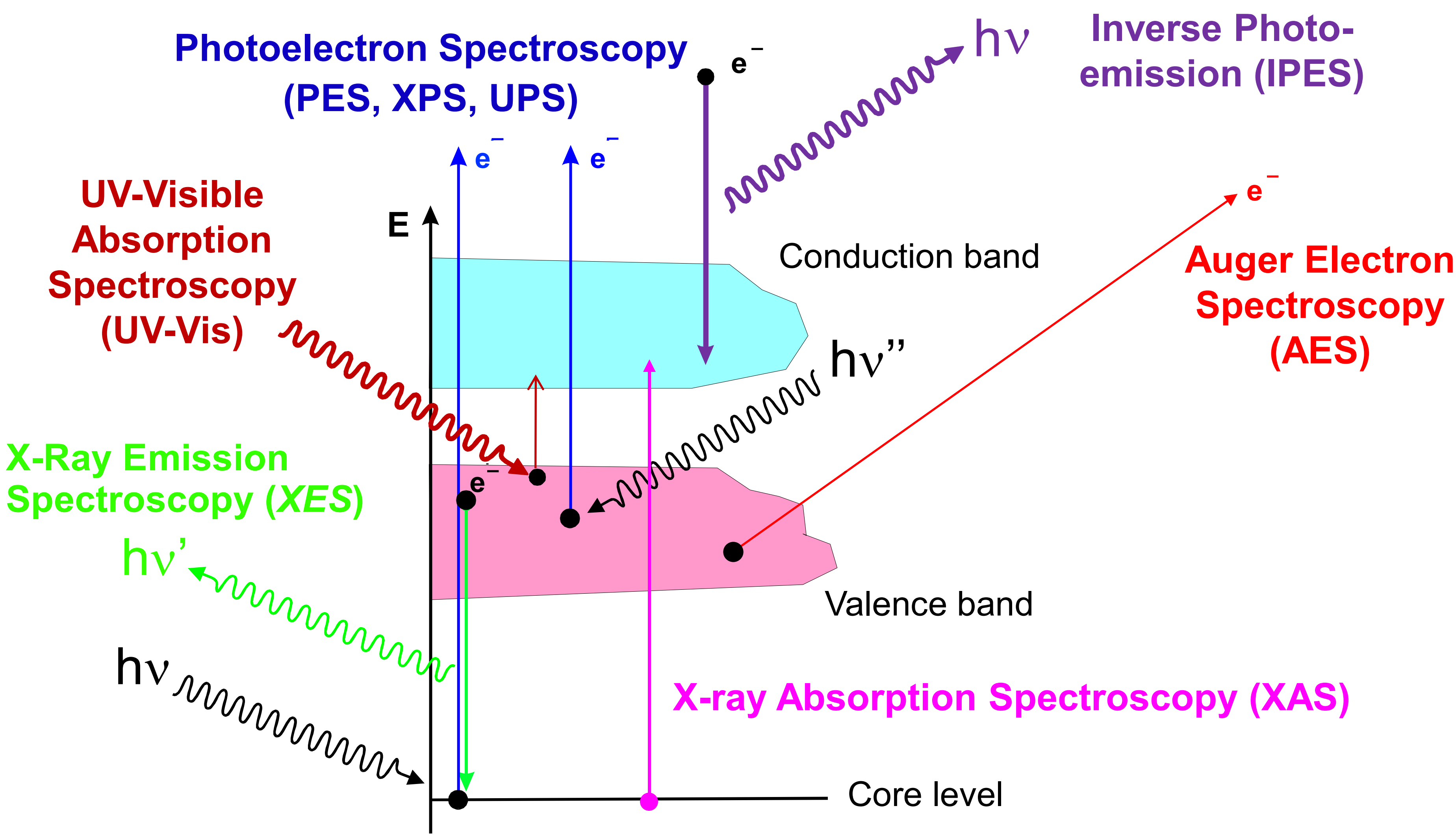
- **Advanced Characterization Support :** ***III-V, Sulfides, Oxides***
- **III-V Surface Validation**

DOE Targets: >1000h @STH > 8% (2013)

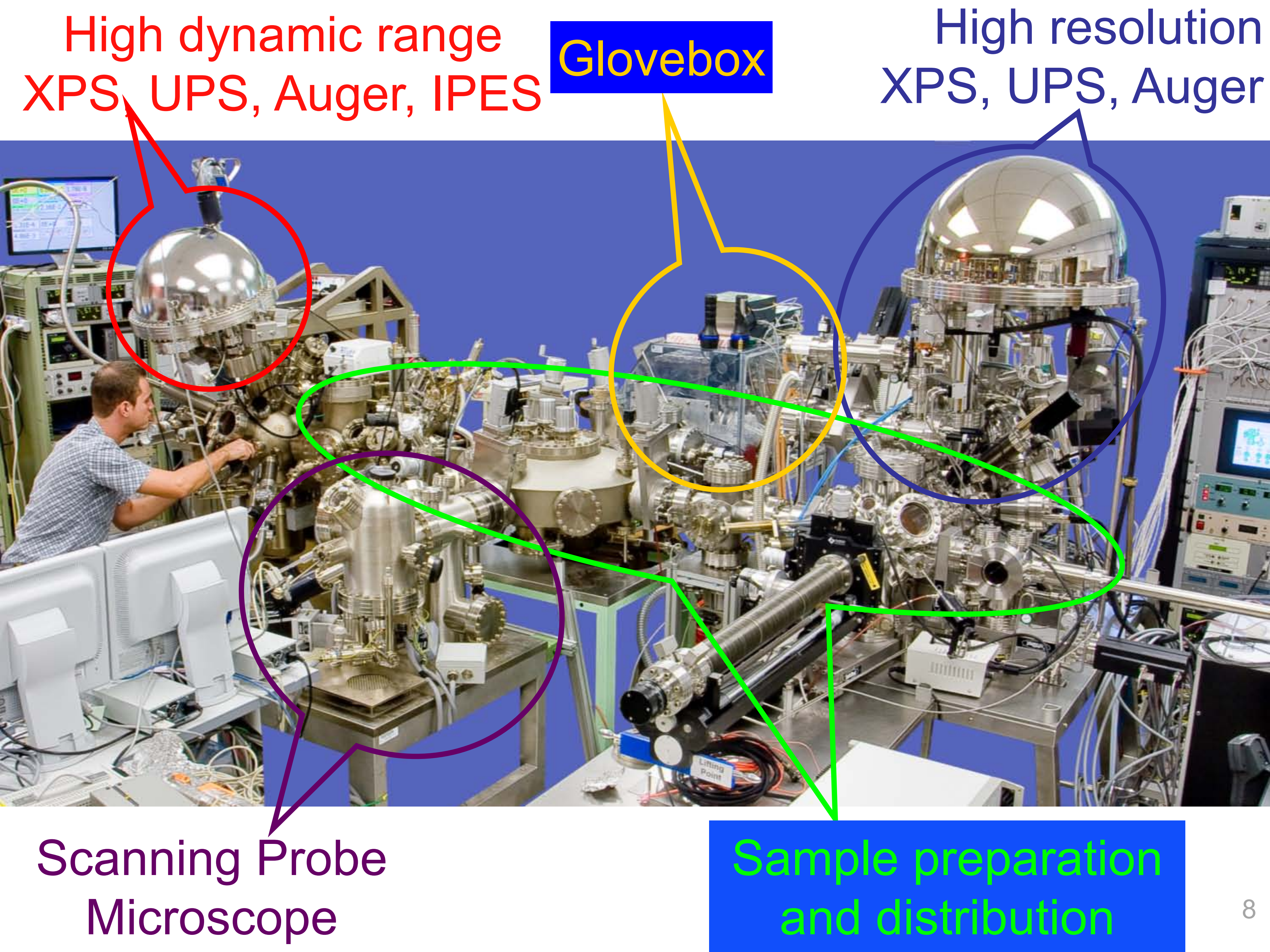
\$2 - 4/kg H_2 projected PEC cost

(beating >\$10/kg H_2 for PV-electrolysis)

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

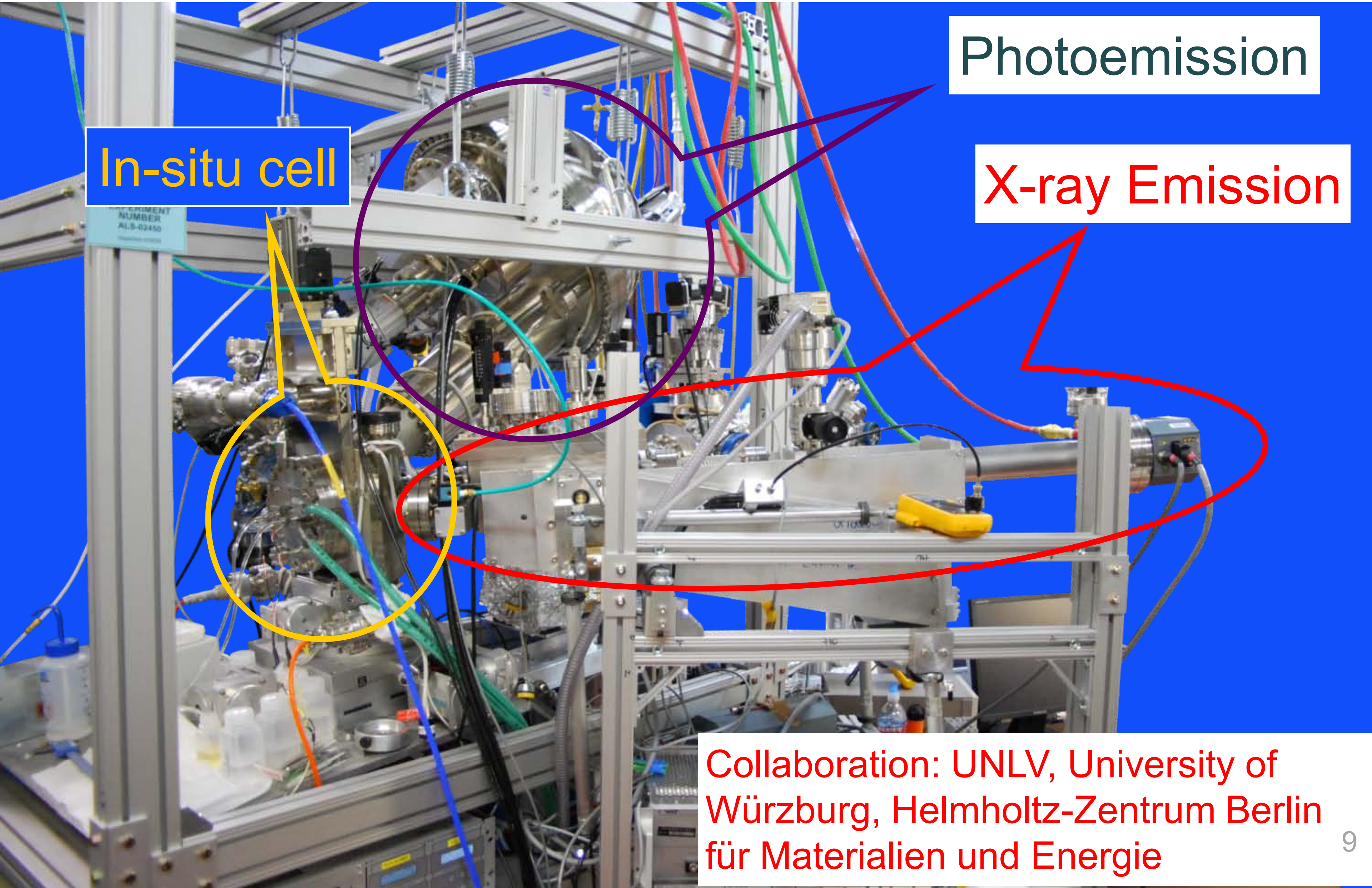


Plus: Atomic Force Microscopy



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

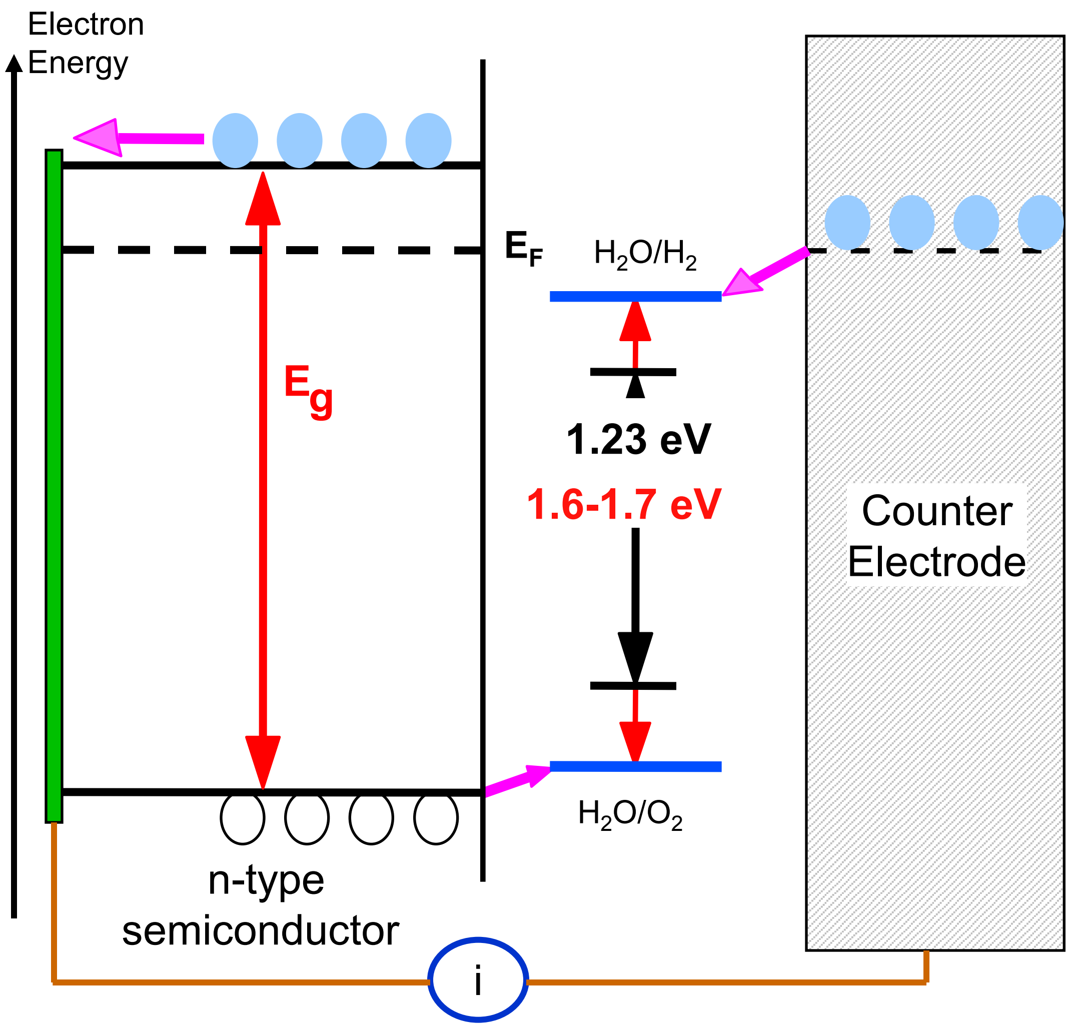
SALSA: Solid And Liquid Spectroscopic Analysis at Beamline 8.0, Advanced Light Source, LBNL



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 <u>simultaneously</u>

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!)

$(Ga,In)_xP_y$ thin films for PEC

With:

Todd Deutsch and John Turner
National Renewable Energy Laboratory

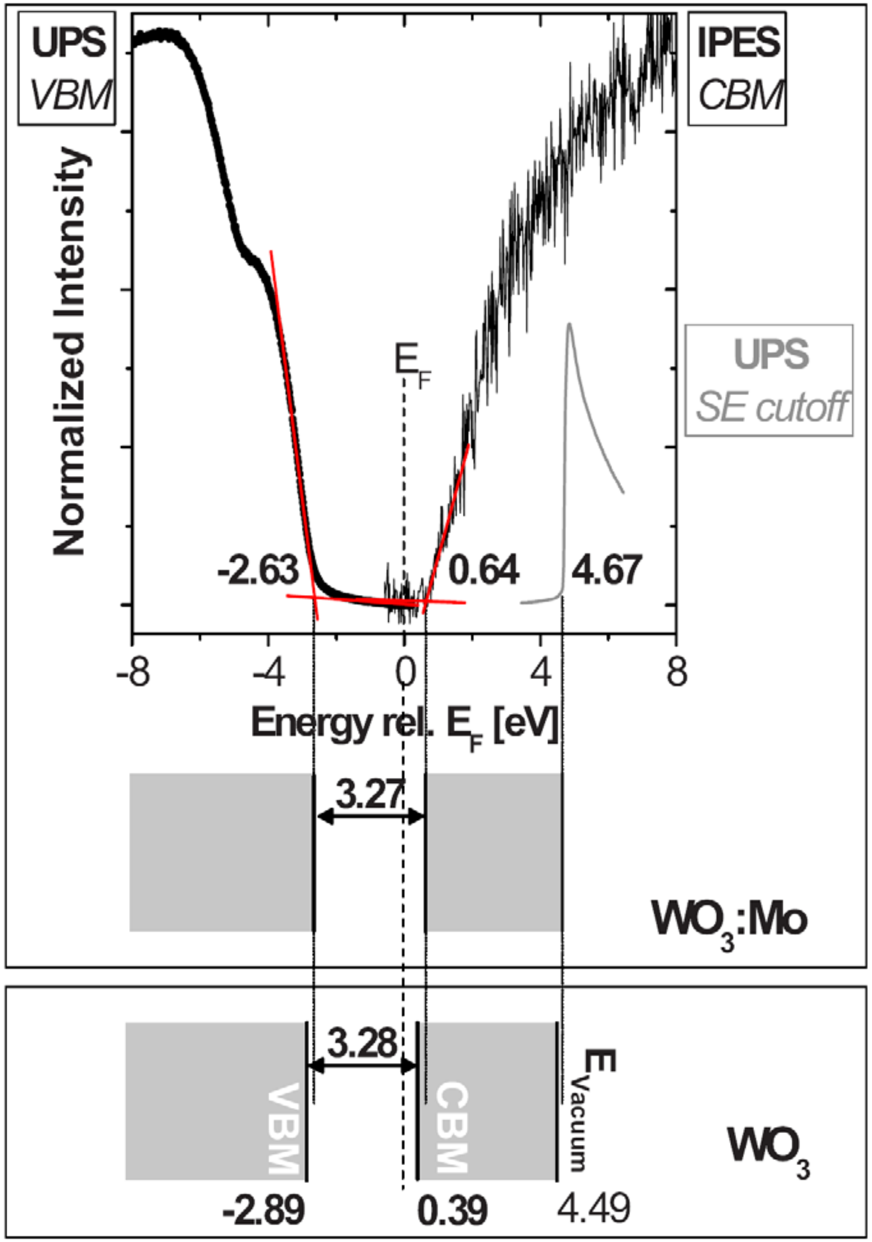
Tadashi Ogitsu and Brandon Wood
Lawrence Livermore National Laboratory

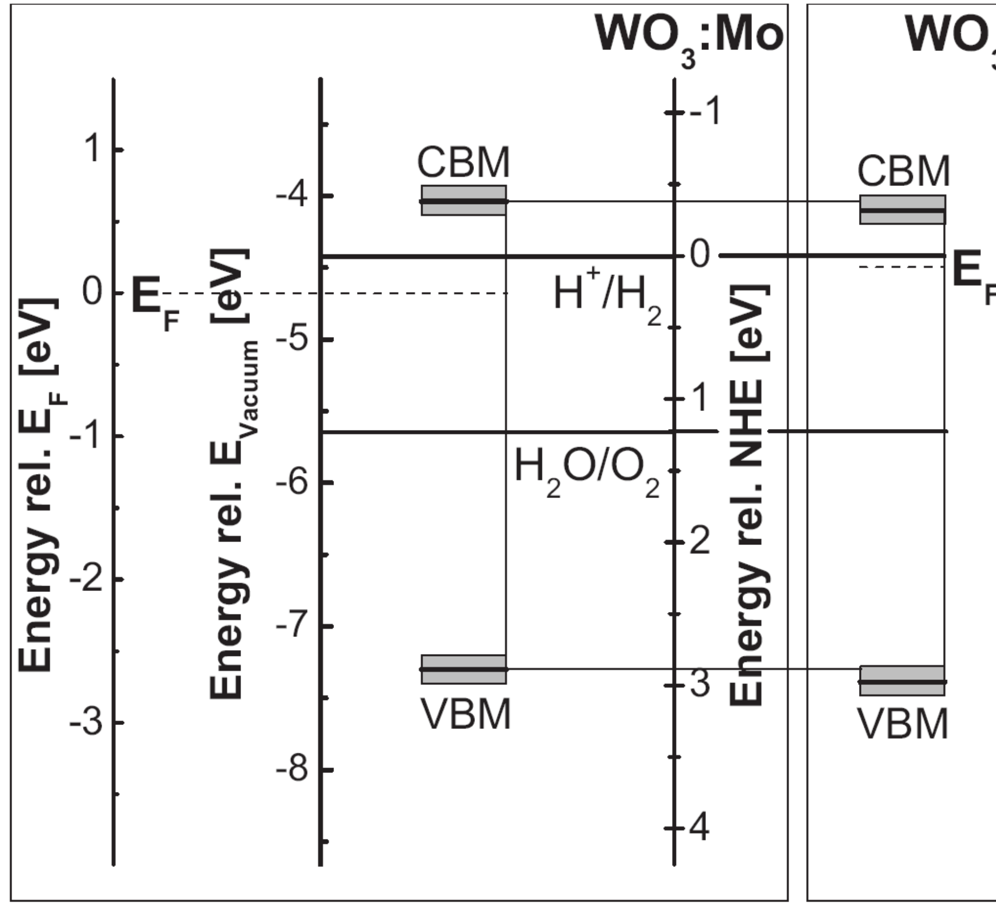
David Prendergast
Lawrence Berkeley National Laboratory

For more details, please see PD035 and PD058

Motivation: compile data for $(Ga,In)_xP_y$ similar to previous results on WO_3 and WO_3:Mo

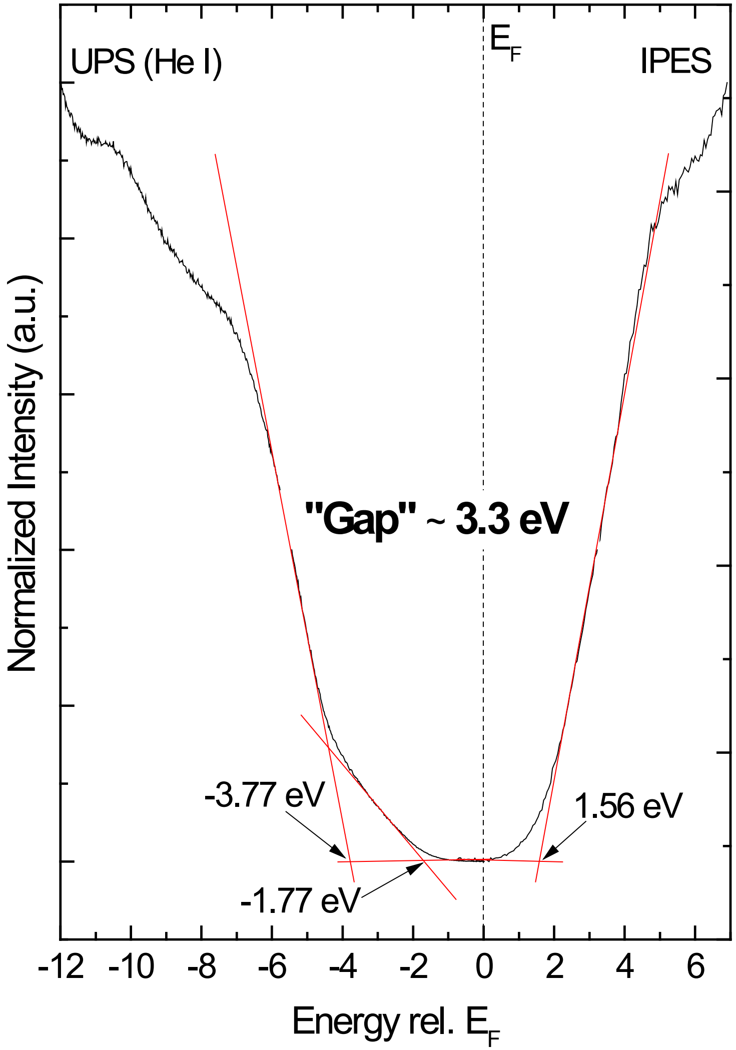
(FY 2010 Accomplishments)

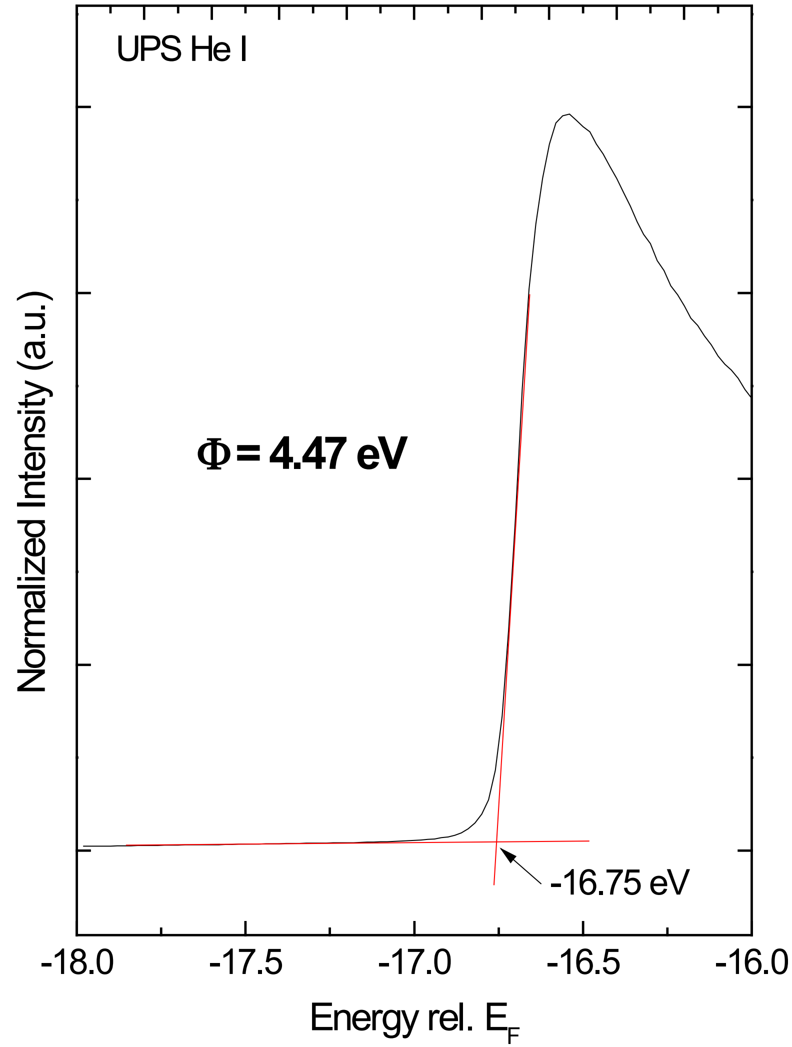




APL **96**, 032107 (2010)

Electronic surface structure of as-received $GaInP_2$ surface ("dirty") *(Accompl.)*

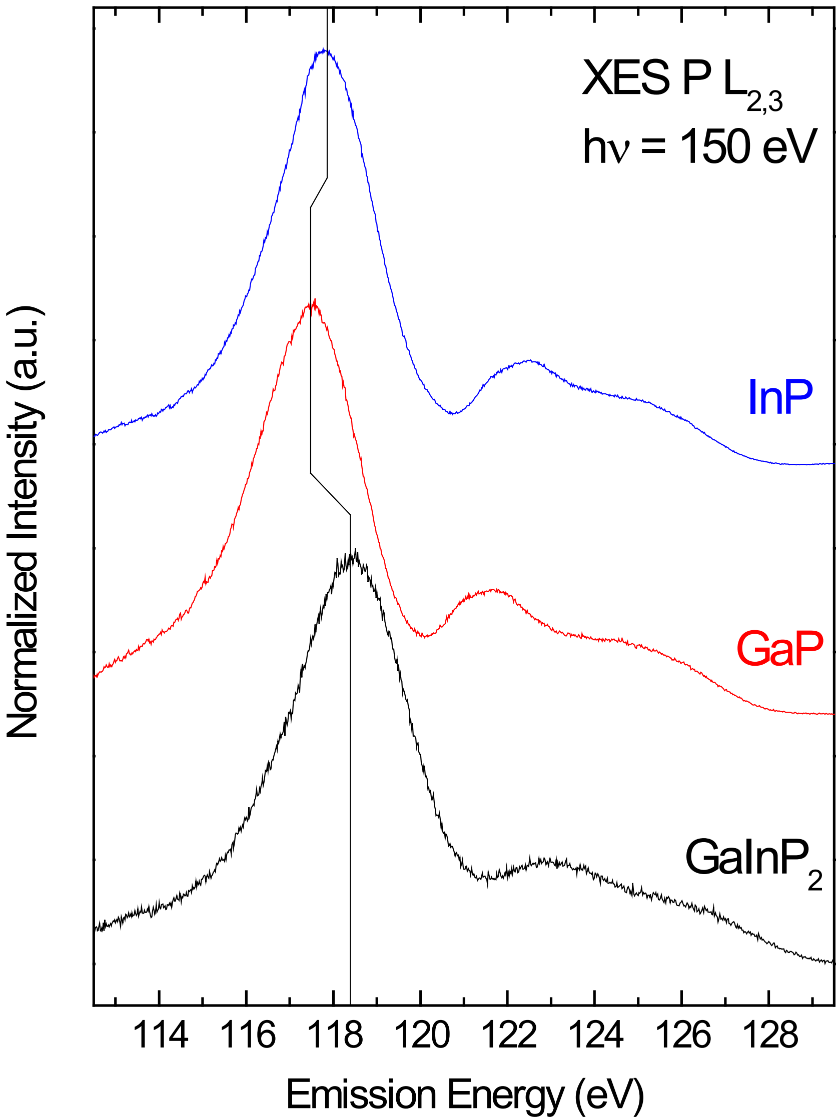




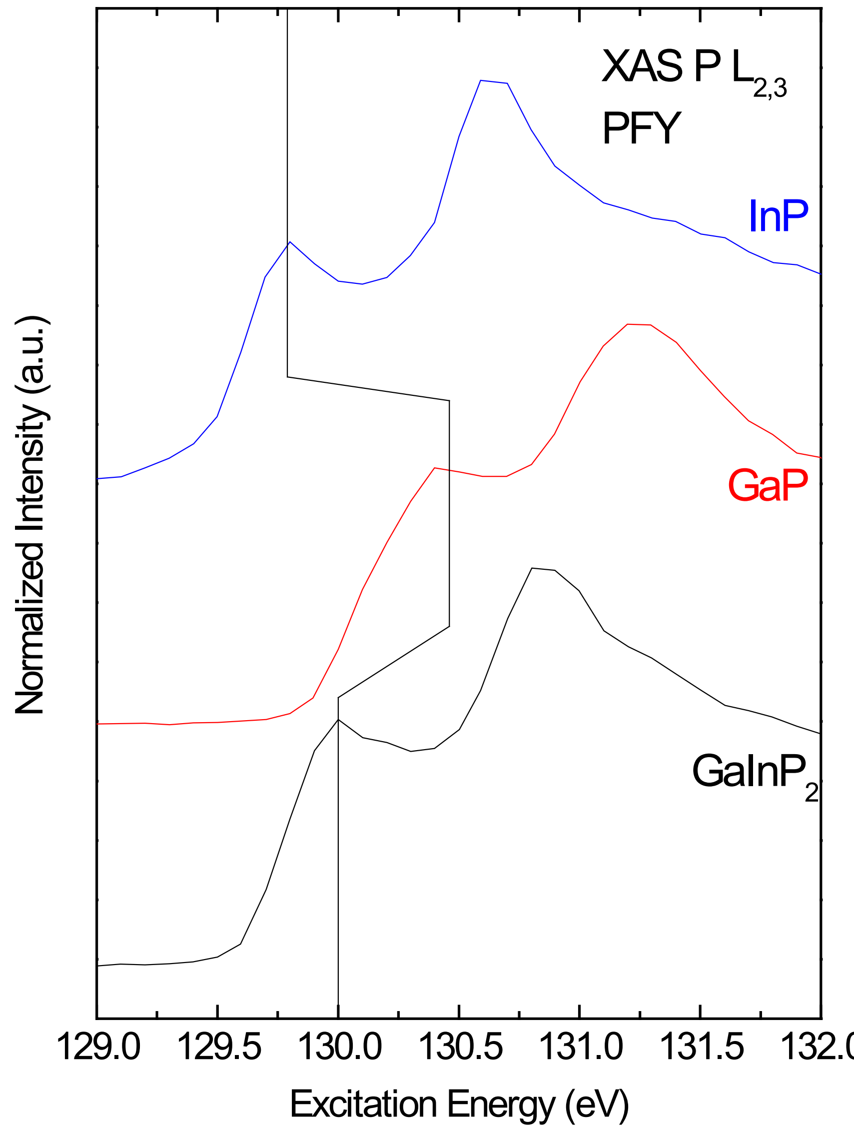
- Surface-sensitive measurements are powerful, but are also influenced by surface adsorbates
- HOMO-LUMO energy separation of surface adsorbates ("band gap"): ~ 3.3 eV
- Compare: UV-Vis and photocurrent spectroscopy (NREL): ~ 1.8 eV
- Work function of surface adsorbates: ~ 4.5 eV
- Current work: optimize surface cleaning procedures to minimize adsorbate influence

XES & XAS of InP, GaP, and GaInP$_2$
(Accomplishments)

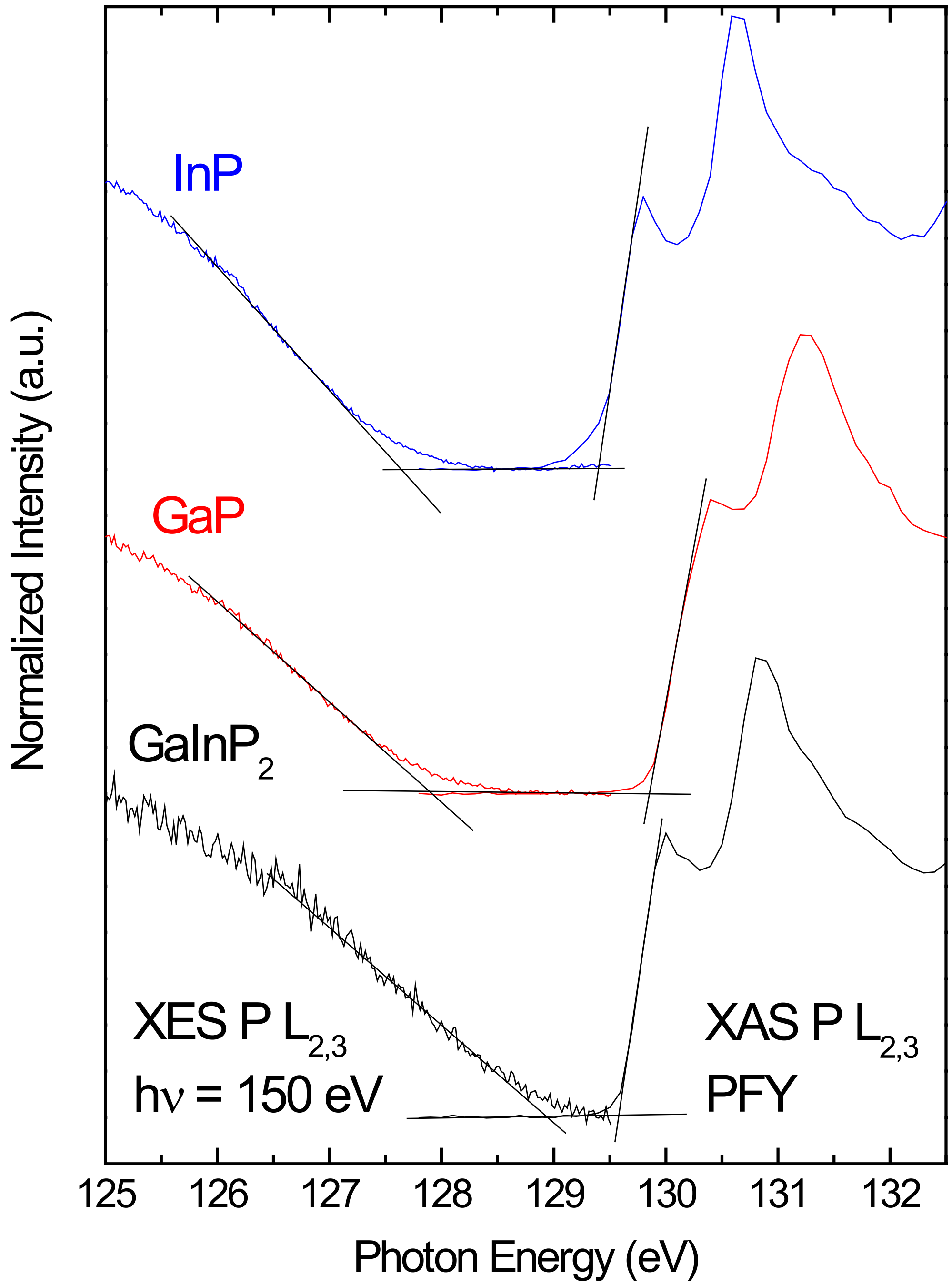
Occupied electronic states



Unoccupied electronic states

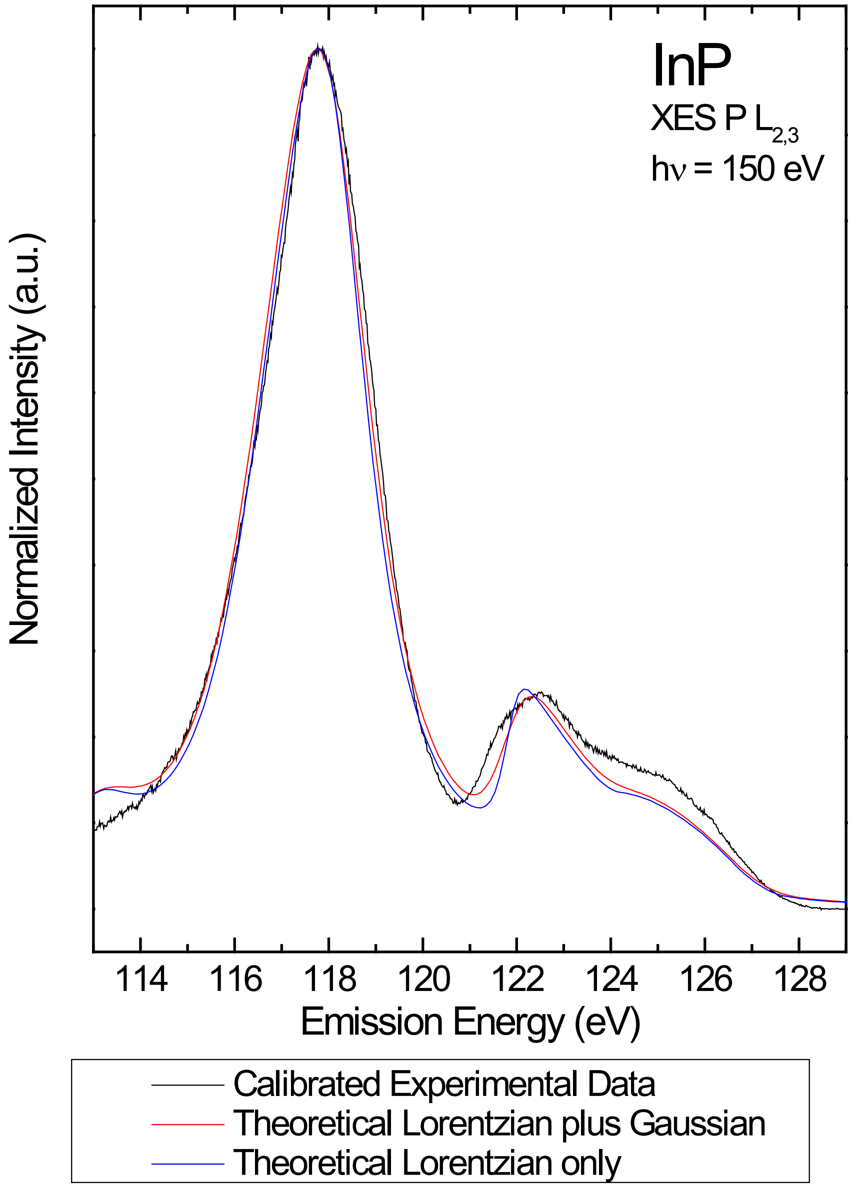


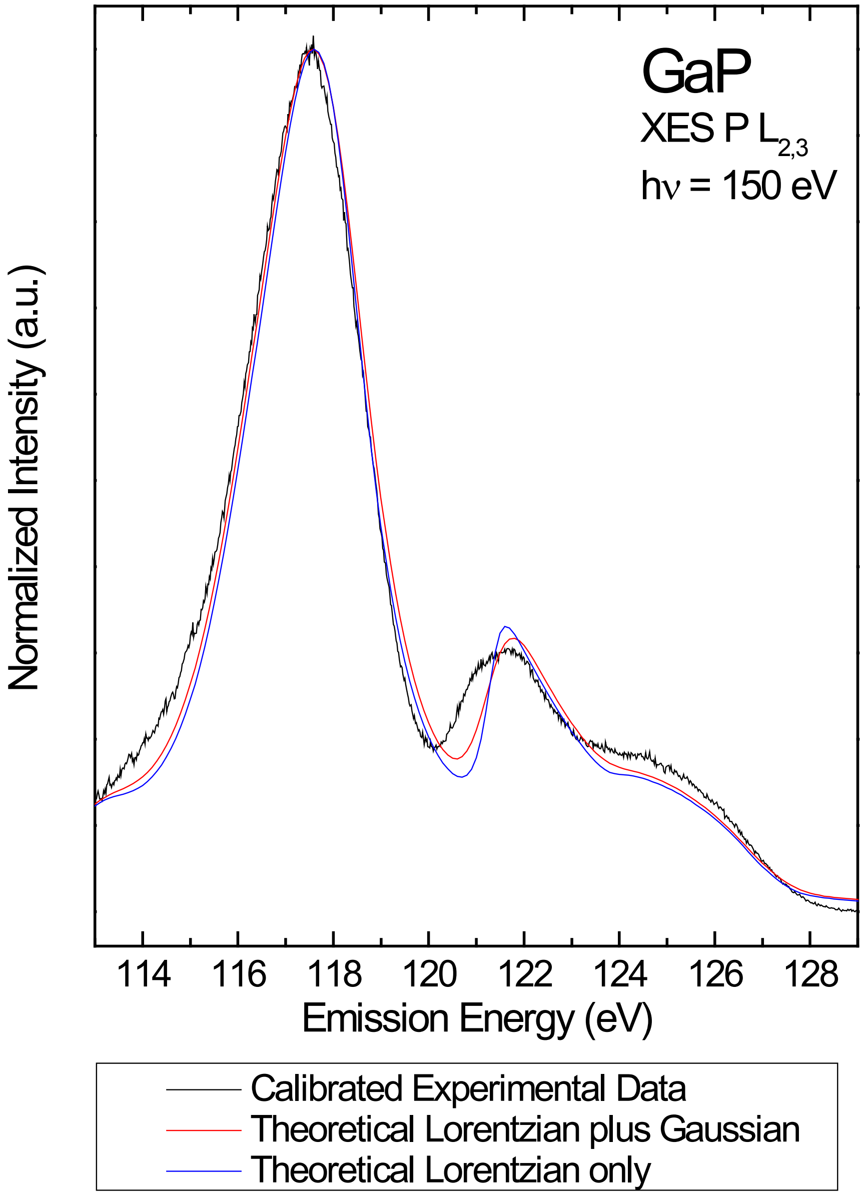
XES & XAS of InP, GaP, and $GaInP_2$ (Accomplishments)



- Lower bound for electronic surface-near bulk band gap can be determined
  - Needs to take core-exciton and spin-orbit splitting (0.84 eV) into account
- Derived lower-bound band gaps:
  - InP: 2.6 eV (Lit: 1.34 eV)
  - GaP: 2.8 eV (Lit: 2.46 eV)
  - $GaInP_2$: 1.5 eV (1.75 eV)
- Needs theory (and cleaner samples) for better understanding

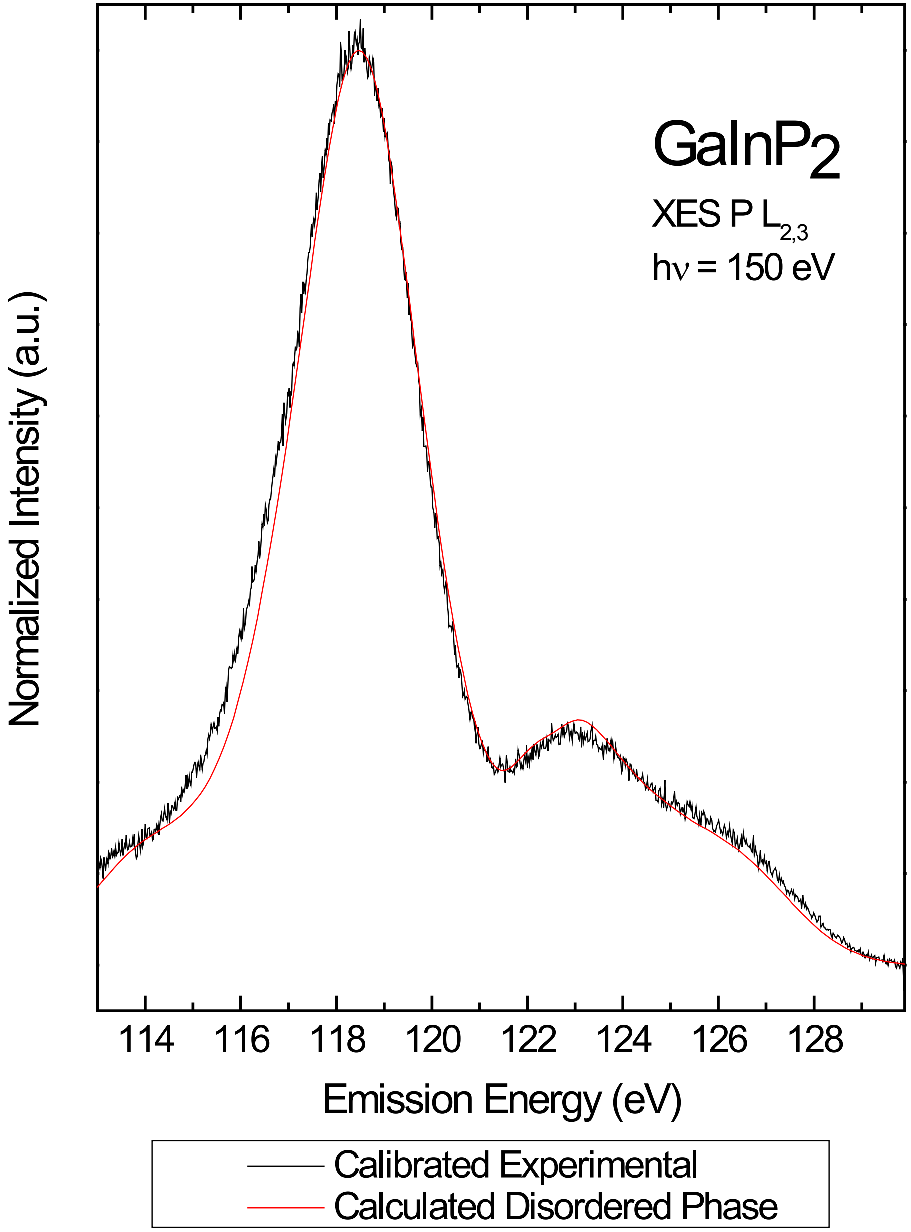
XES: Comparison of Theory and Experiment (Accompl.)





Theoretical spectra include matrix elements and were shifted to align with experiment

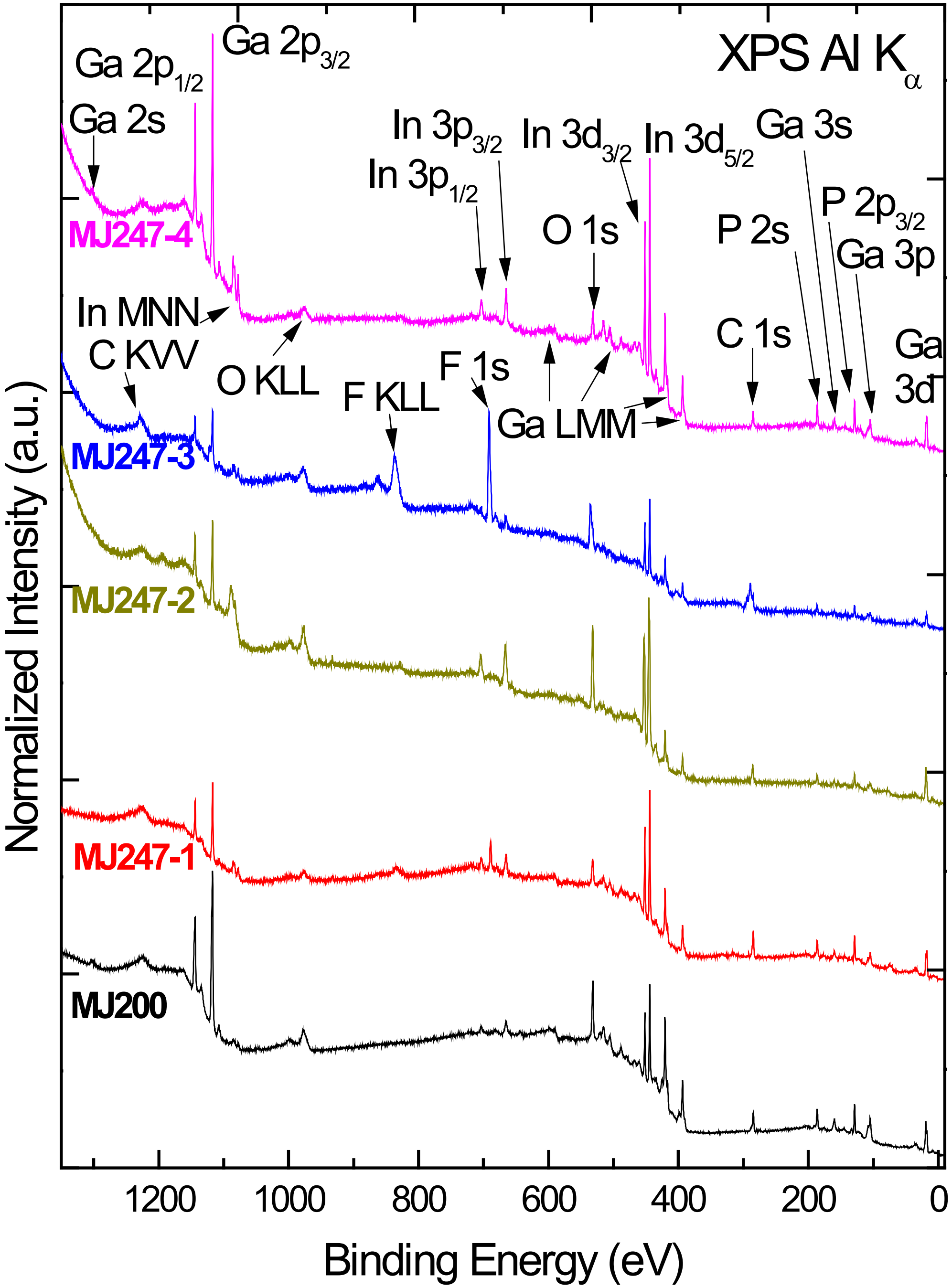
XES: Comparison of Theory and Experiment (Accompl.)



- Excellent agreement between theory and experiment for all three compounds (InP, GaP, $GaInP_2$)
- Further refinement necessary
- Will allow us to derive exact position of VBM by comparing experiment and theory
- Next step: comparison of XAS experiment and theory

Theoretical spectra include matrix elements and were shifted to align with experiment

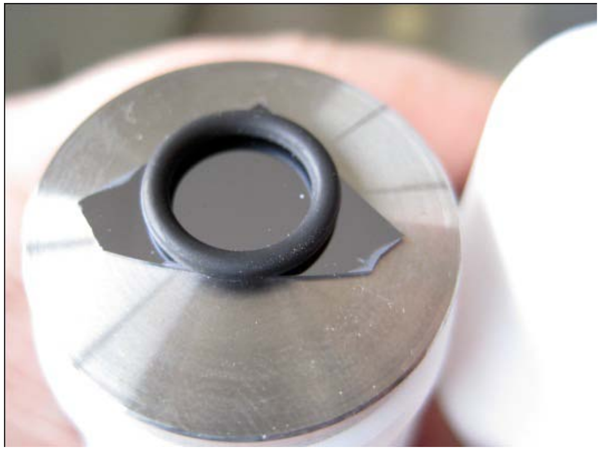
XPS analysis of tested $GaInP_2$ samples: Survey Spectra (Accomplishments)



Sample	Treatment	Electrolyte
MJ247-4	30 second etch in conc. sulfuric acid	
MJ247-3	$-8mA/cm^2$, 22hrs, AM1.5G	0.1M HNO_3 +0.5M NH_4NO_3 w/ Zonyl® FSN-100
MJ247-2	$-8mA/cm^2$, 22hrs, AM1.5G	1M KOH w/ Zonyl® FSN-100
MJ247-1	$-8mA/cm^2$, 22hrs, AM1.5G ($+8mA/cm^2$ applied for ~1 sec prior to run)	0.5M H_2SO_4 w/ Zonyl® FSN-100
MJ200	as-grown	

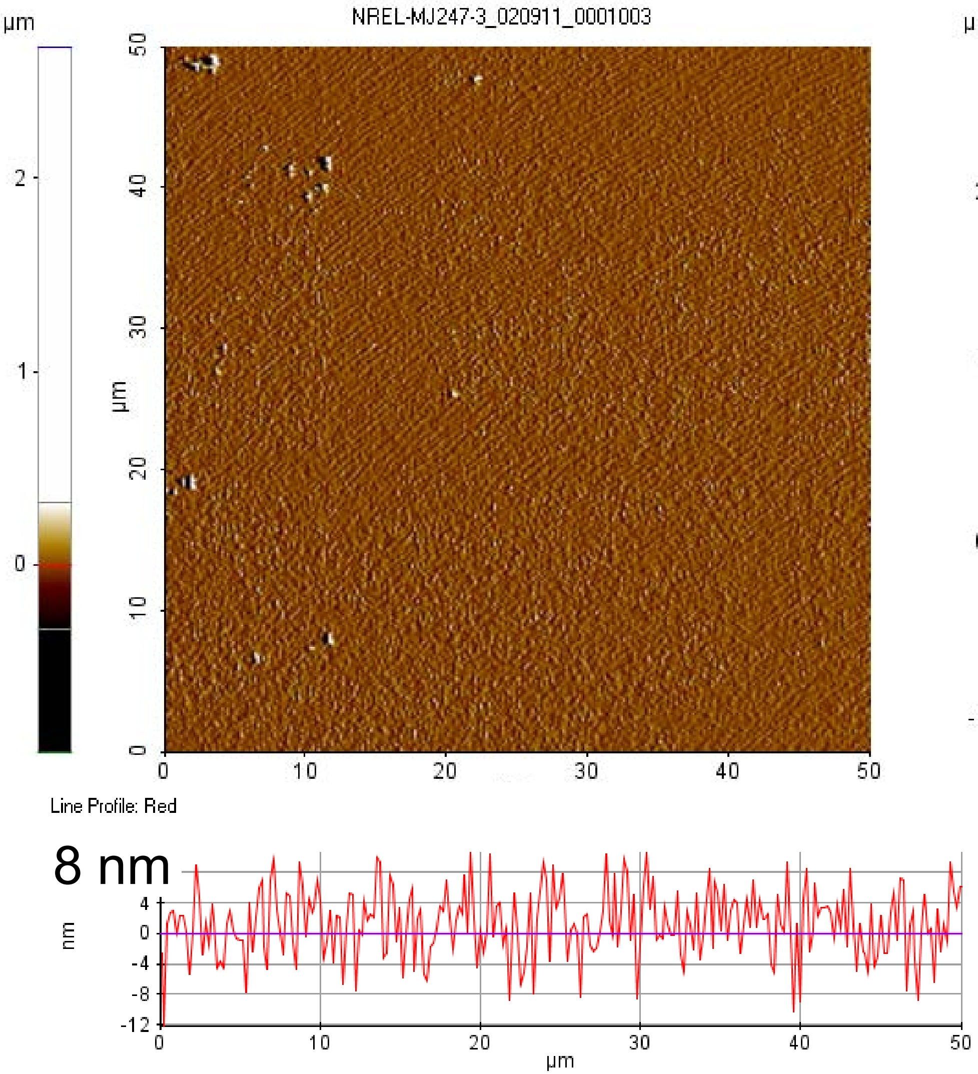
Atomic Force Microscopy (chemical stability) of a tested $GaInP_2$ surface (Accomplishments)

Sample	Treatment	Electrolyte
MJ247-3	$-8 mA/cm^2$, 22 hrs, AM1.5G	0.1M HNO_3 +0.5M NH_4NO_3 w/ Zonyl FSN-100

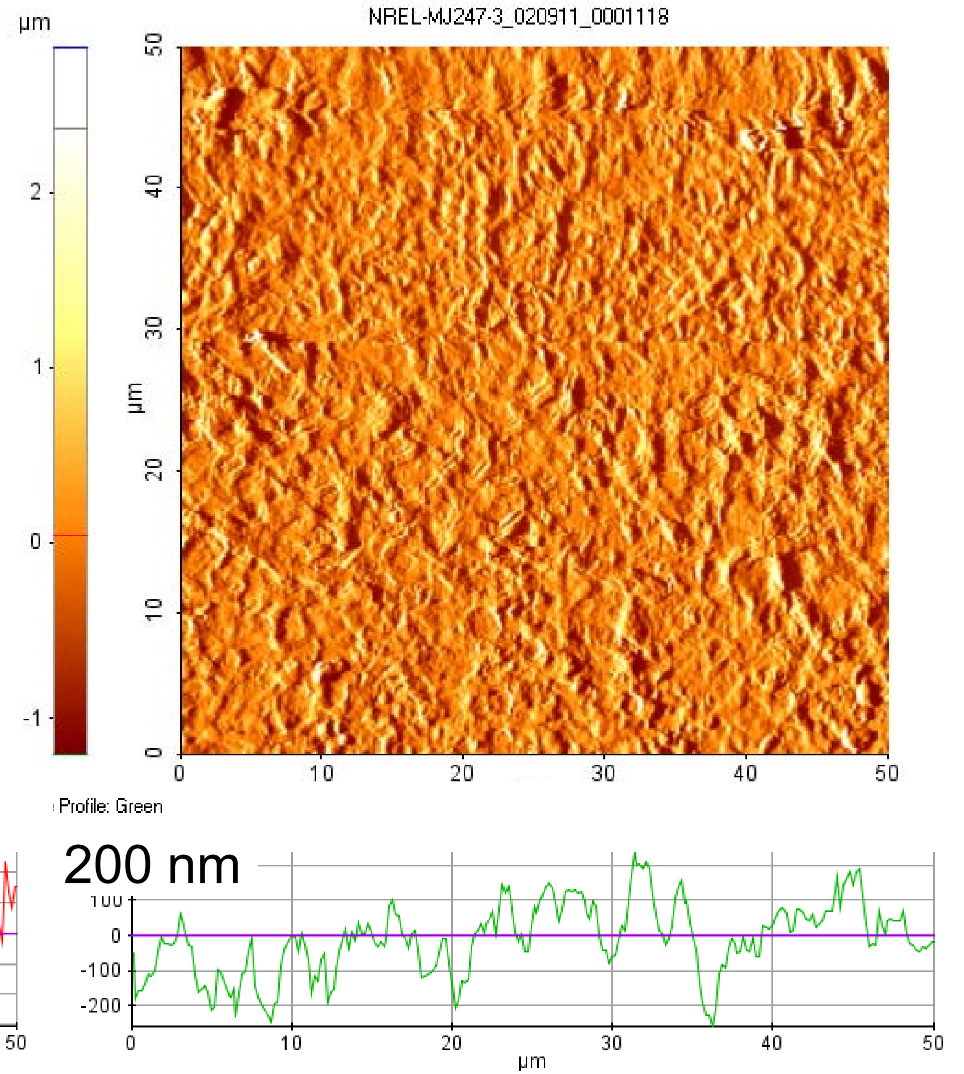


Impact of Exposure to Electrolyte (Accomplishments)

Unexposed Region

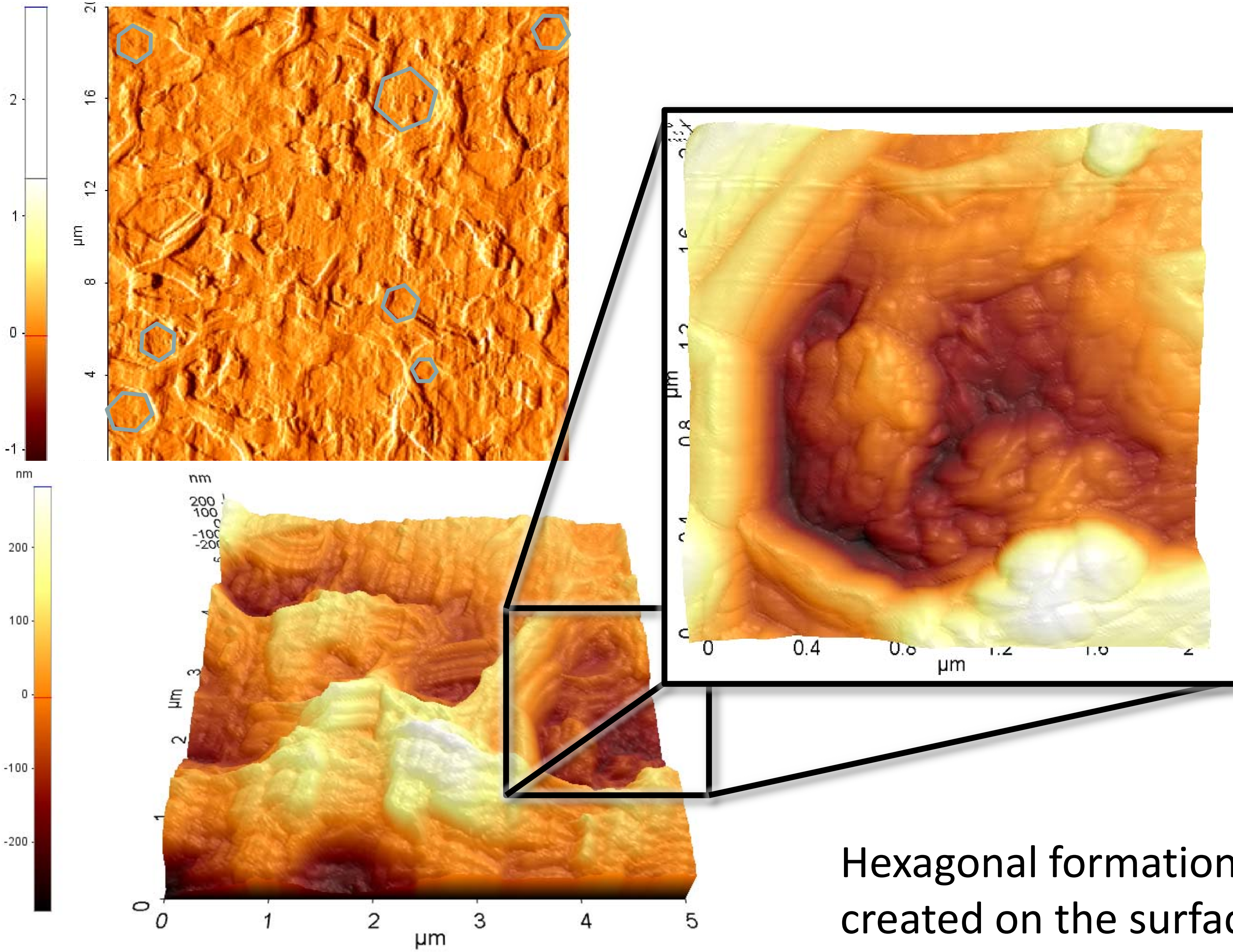


Exposed Region



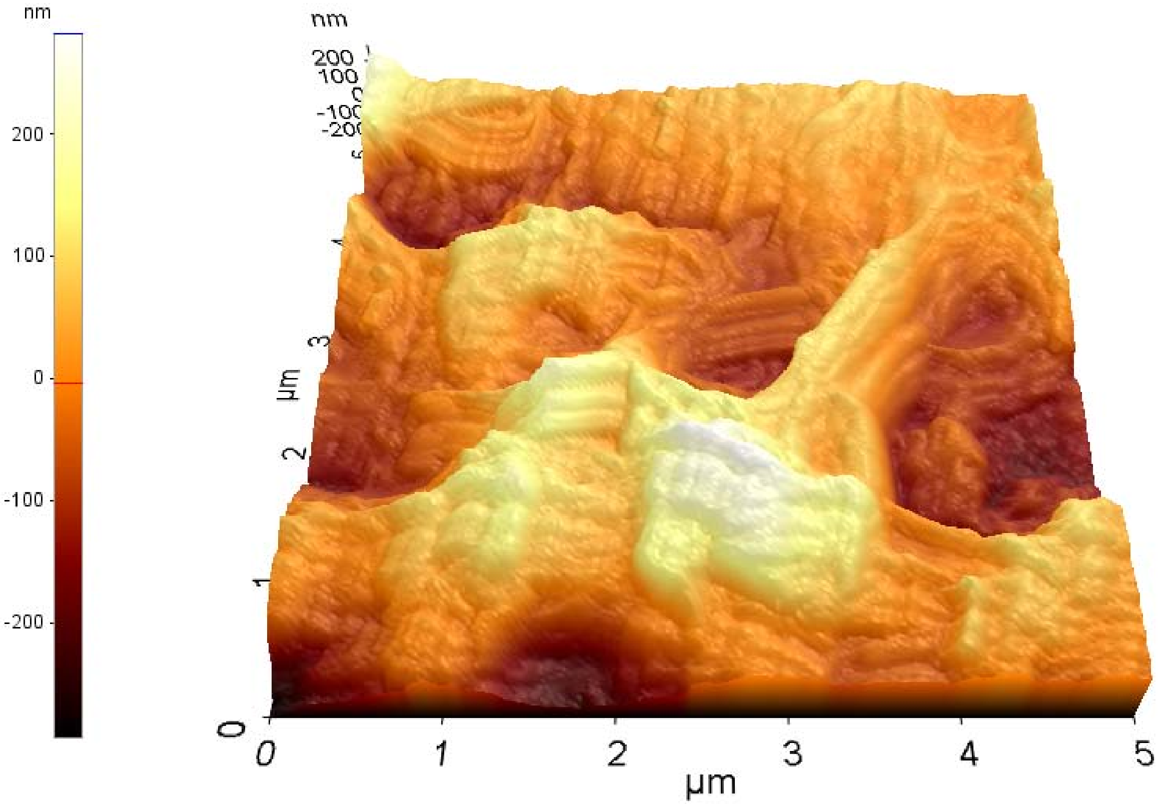
- The region of the sample exposed to electrolyte exhibits surface roughness not seen in the unexposed region
- The exposed region is highly corrugated, whereas the unexposed region is flat and appears ordered

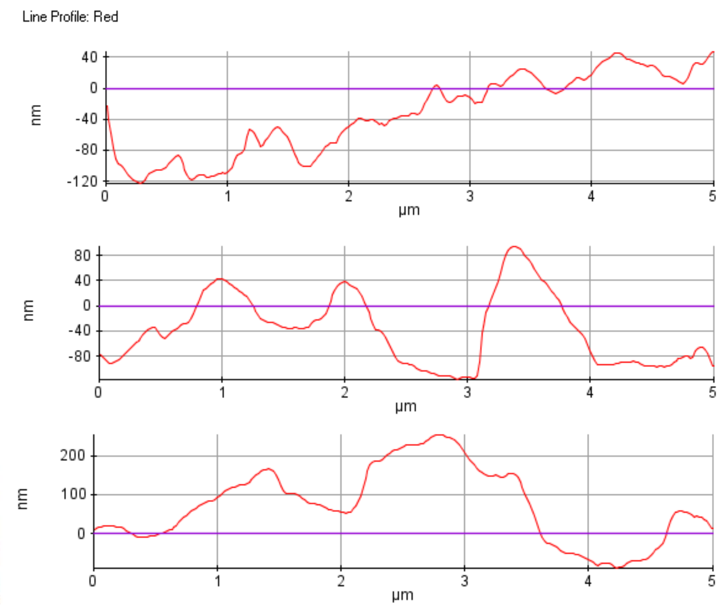
Impact of Exposure to Electrolyte (Accomplishments)



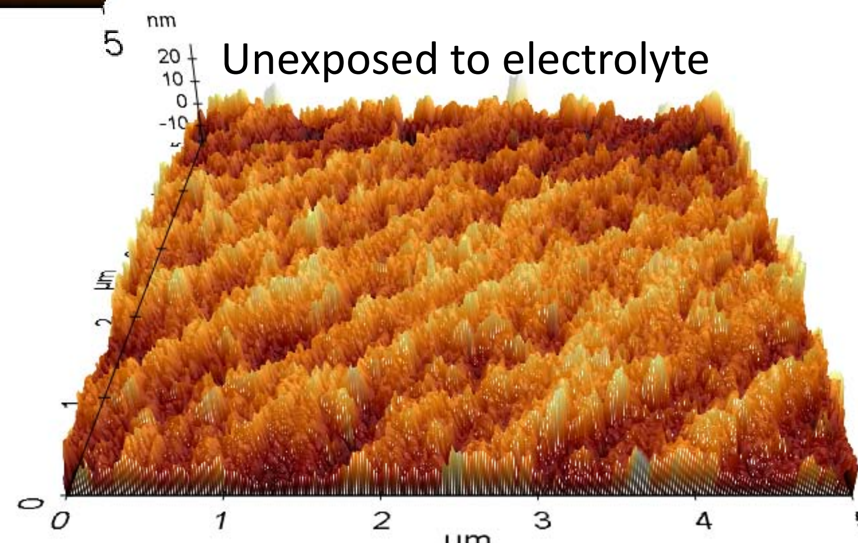
Hexagonal formations are created on the surface

Comparison: Before/After Exposure (Accomplishments)

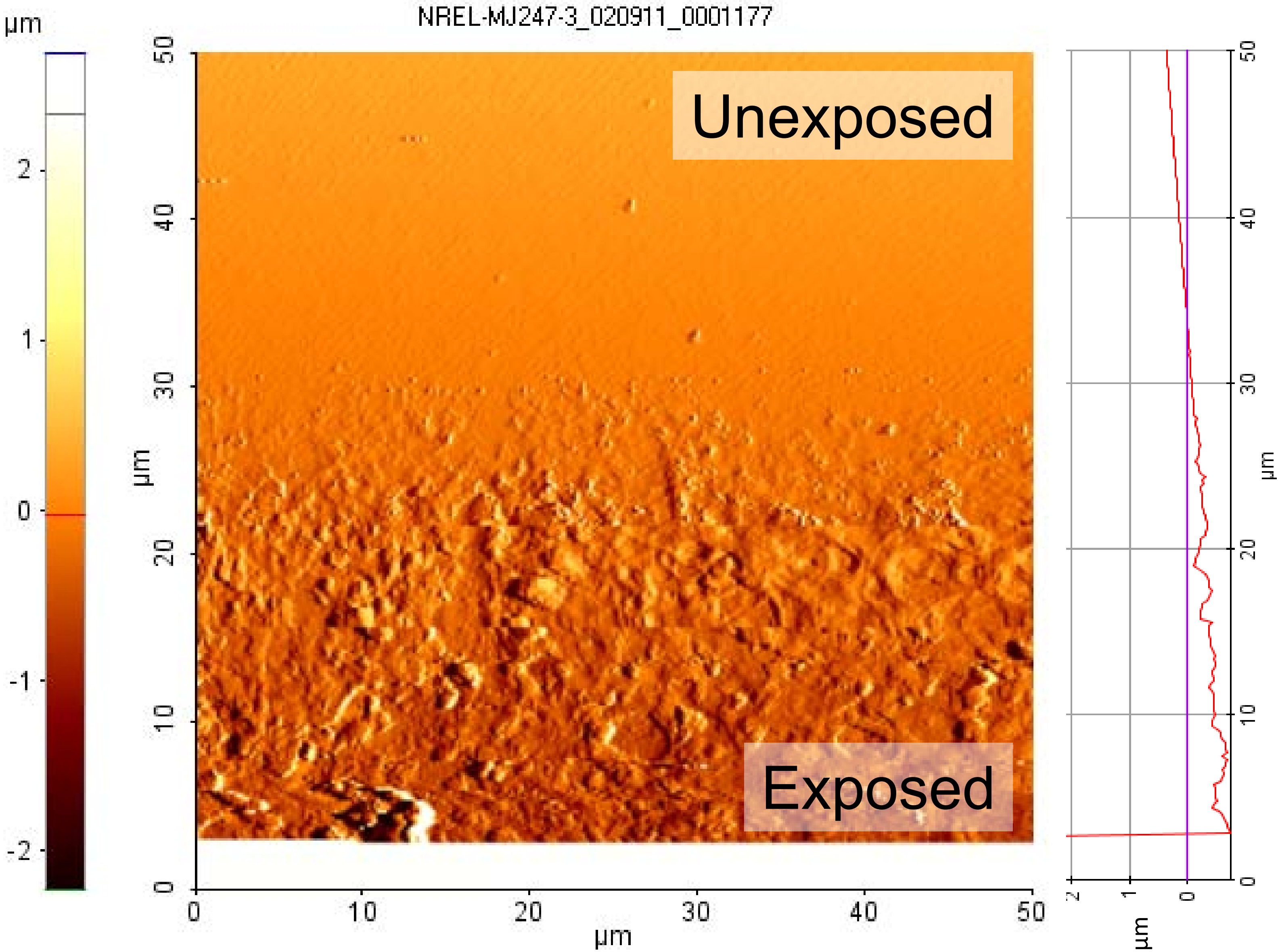




- Erosion or etching appears to have exposed a skeletal framework
- Unexposed regions show a row-like structure (step edges?)



Transition Region (Accomplishments)



- Interface between the exposed and unexposed regions shows that surface roughness of the unexposed region is due to erosion, not the deposition of material onto the surface

$(Ga,In)_xP_y$ Summary (Accomplishments)

- First band gap determination experiments
  - Surfaces: need optimized surface cleaning
  - Bulk: XES/XAS derives 1.5 eV – needs correlation with theory (where are the correct band edges?)
  - First comparison of XES theory and experiment yields <u>excellent</u> agreement
- First analysis of electrolyte exposure
  - Chemical changes (XPS)
  - Morphological changes (AFM)
  - Future: spectroscopy *in-situ* (XES/XAS)

MoS_2 nanomaterials for PEC

With:

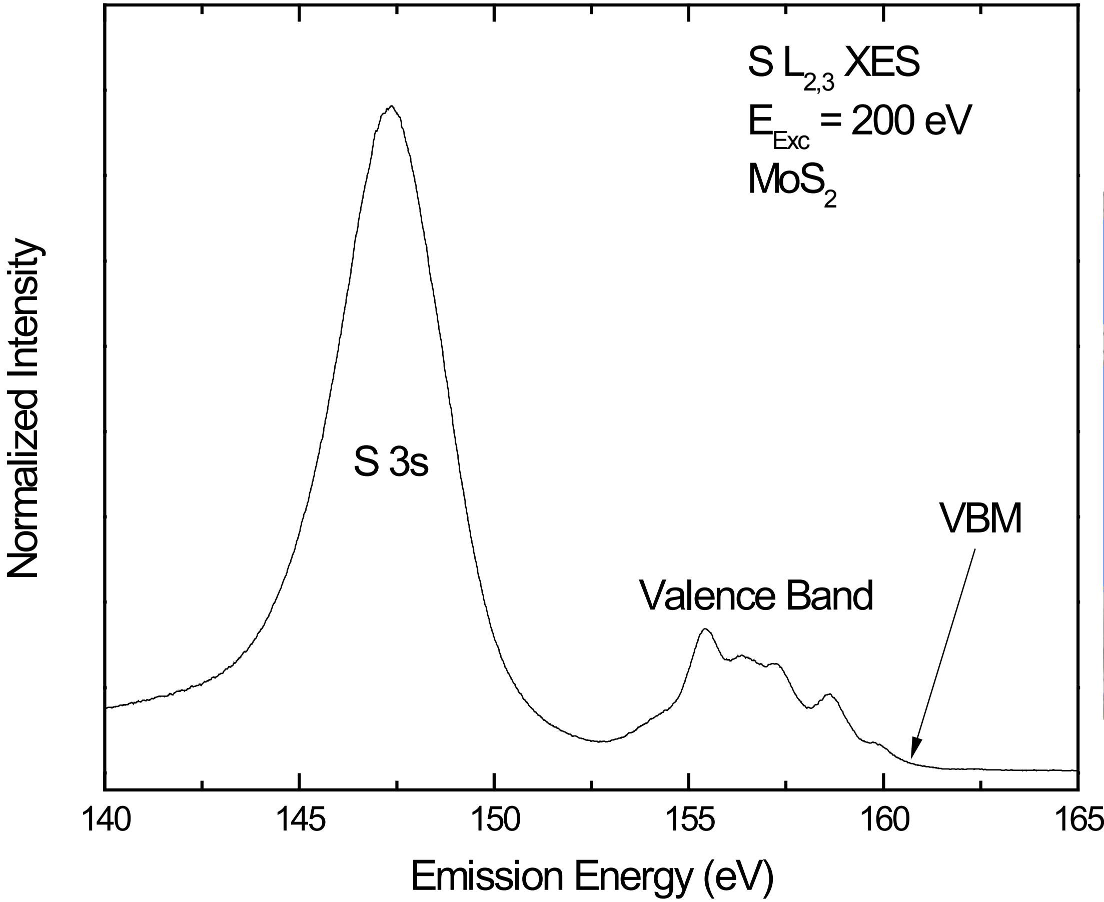
Zhebo Chen and Tom Jaramillo

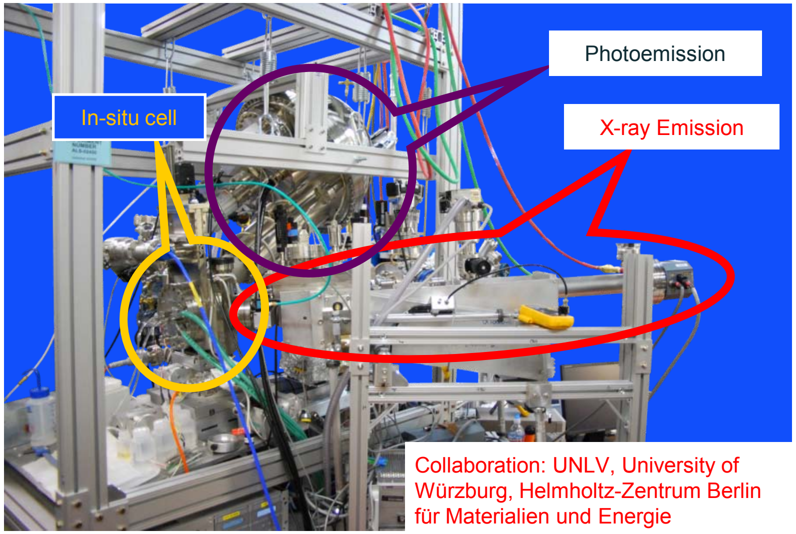
Stanford University

For more details, please see PD033

Very first results *(Accomplishments)*

- Optimized XES spectrometer in SALSA for S $L_{2,3}$ XES (to allow *in-situ* spectroscopy) – MoS_2 reference

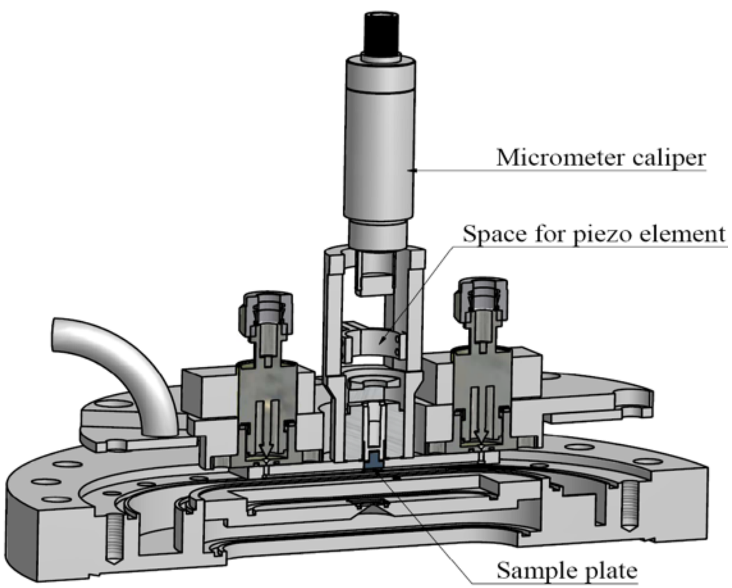


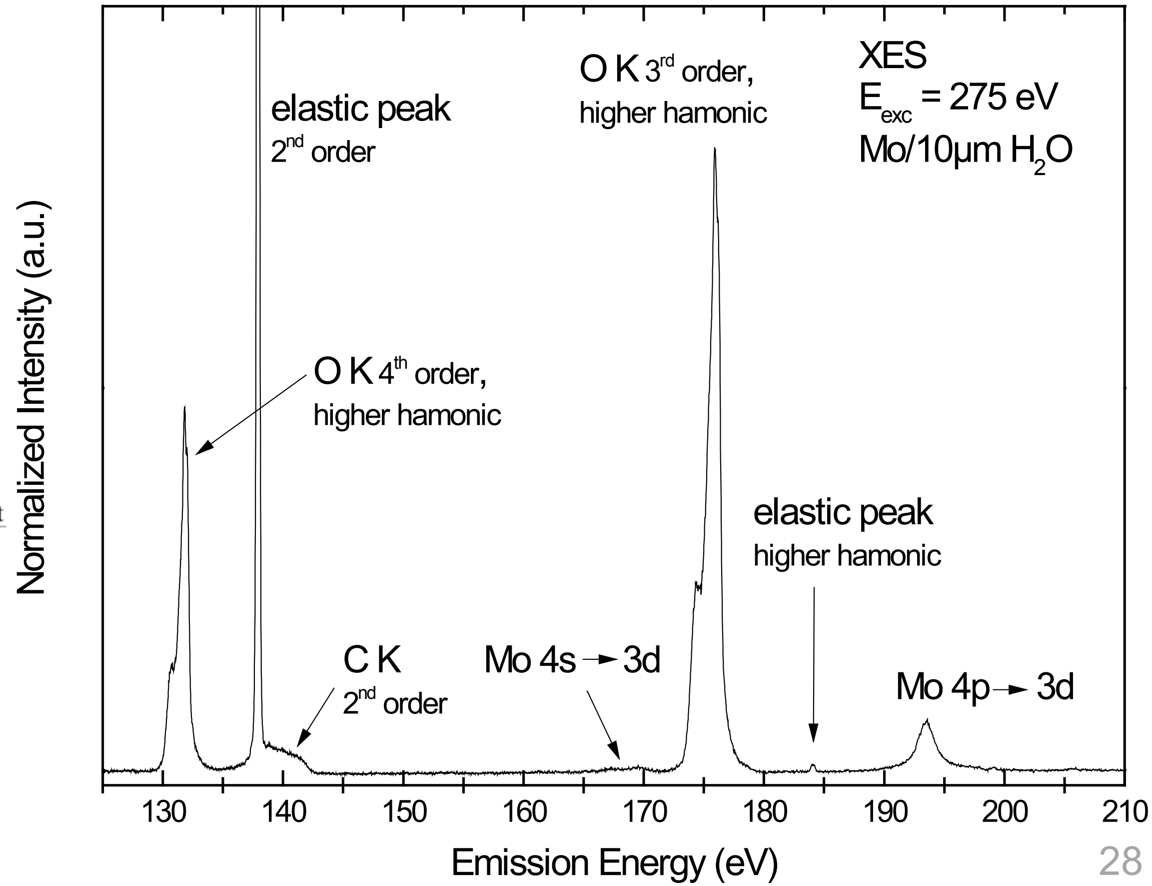


Collaboration: UNLV, University of Würzburg, Helmholtz-Zentrum Berlin für Materialien und Energie

Very first results (Accomplishments)

- Developed prototype liquid-solid interface cell for XES in SALSA (to allow *in-situ* spectroscopy) – Mo metal reference under 10 μm of H_2O





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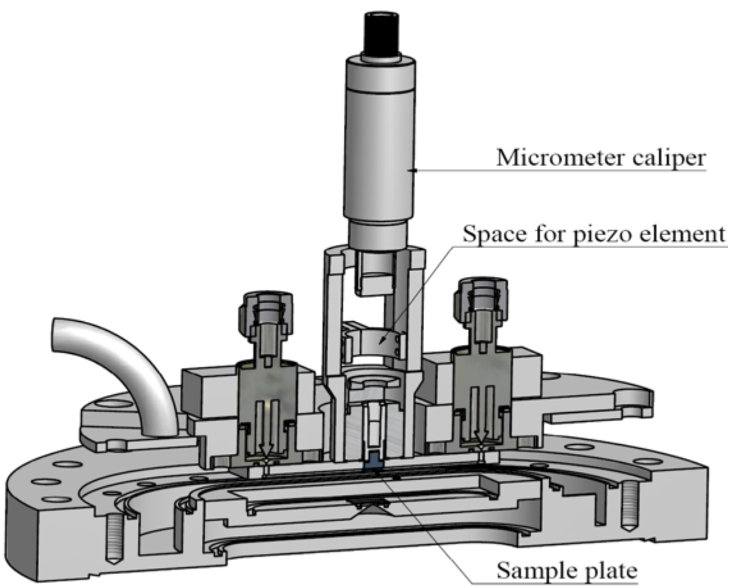

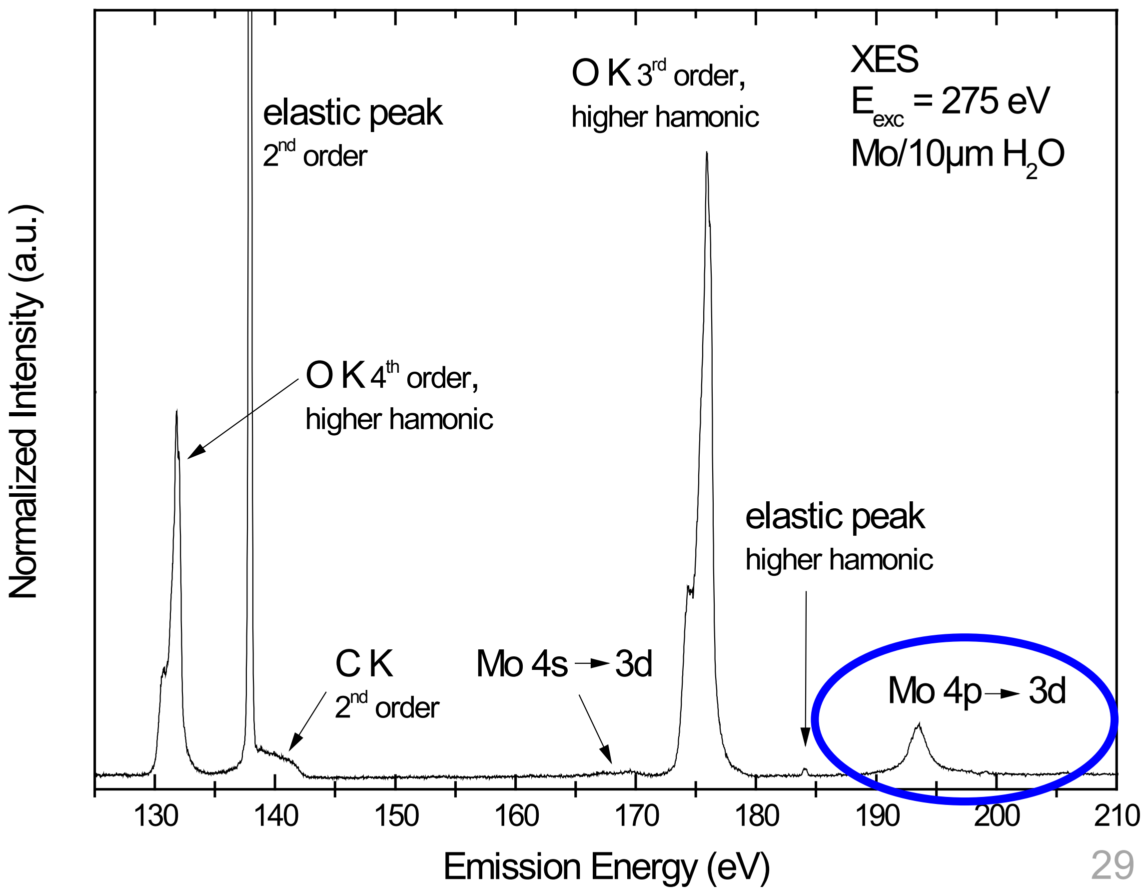

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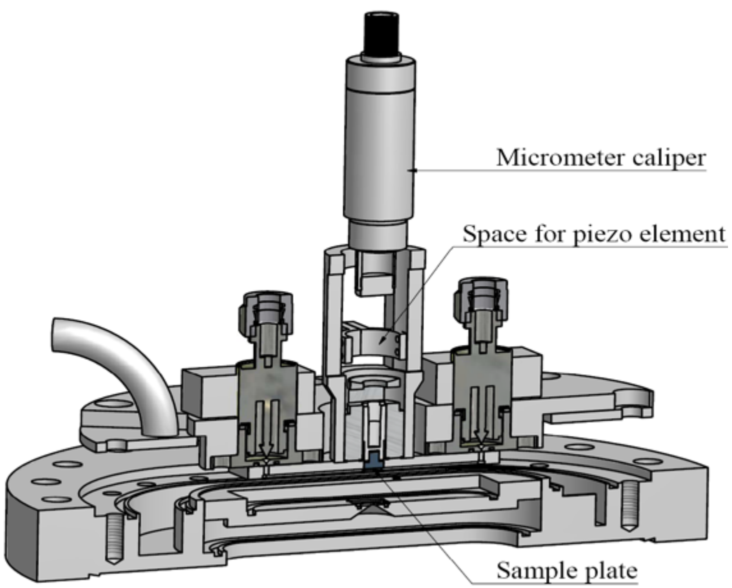
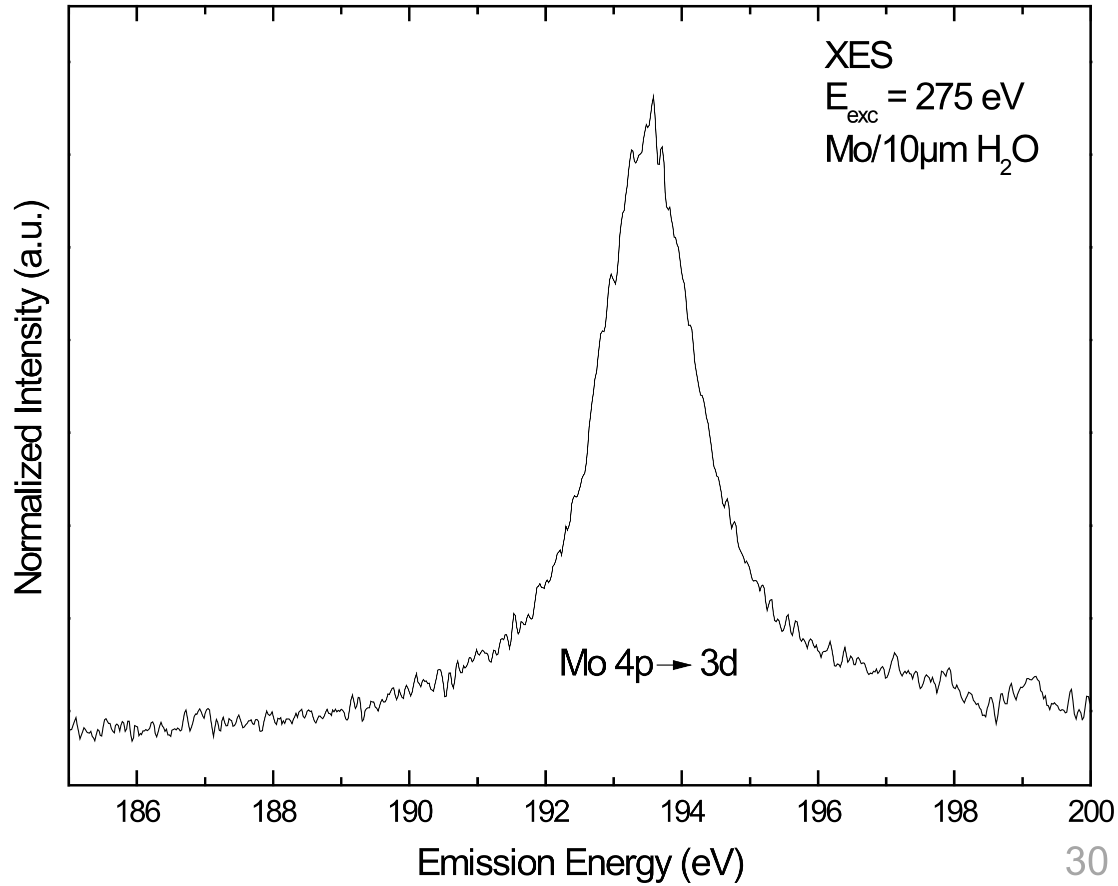




Electronic Structure of Fe_2O_3 Thin Films

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

University of California, Santa Barbara

UCSB

Sample Preparation (Approach)

"Real world" Film
(UCSB)

x nm Fe
Pt (150 nm)
Ti (50 nm)
Quartz wafer

Annealed in air
- 700 C, 4 hr, 2 C/min

→

~2x nm Fe_2O_3
Pt (150 nm)
Ti (50 nm)
Quartz wafer

Prototypical Films
(UNLV)

Fe Foil

Heated in partial O_2
- 600 C, 90 seconds

→

FeO_x

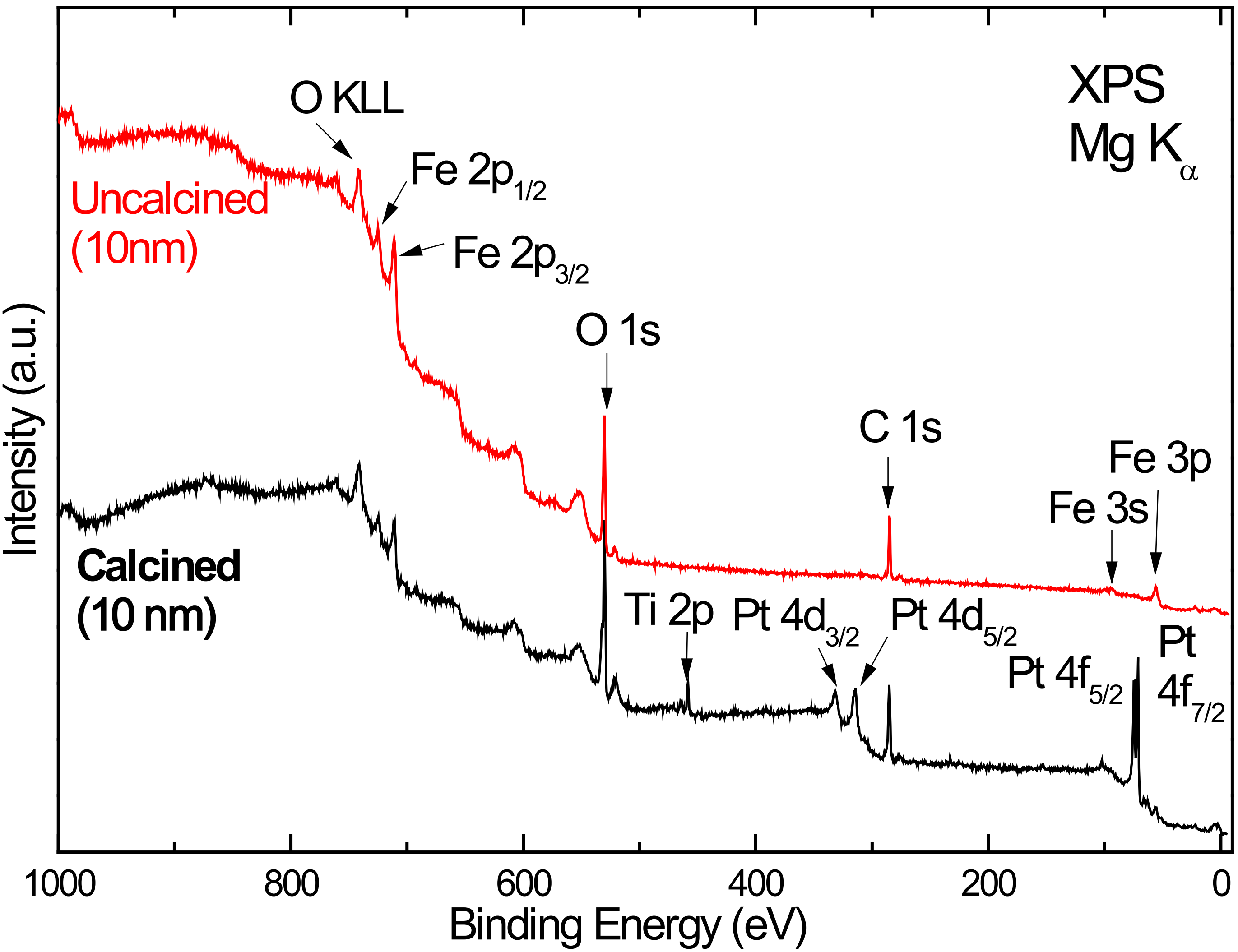
Ti Foil

Heated in partial O_2
- 600 C, 3 minutes

→

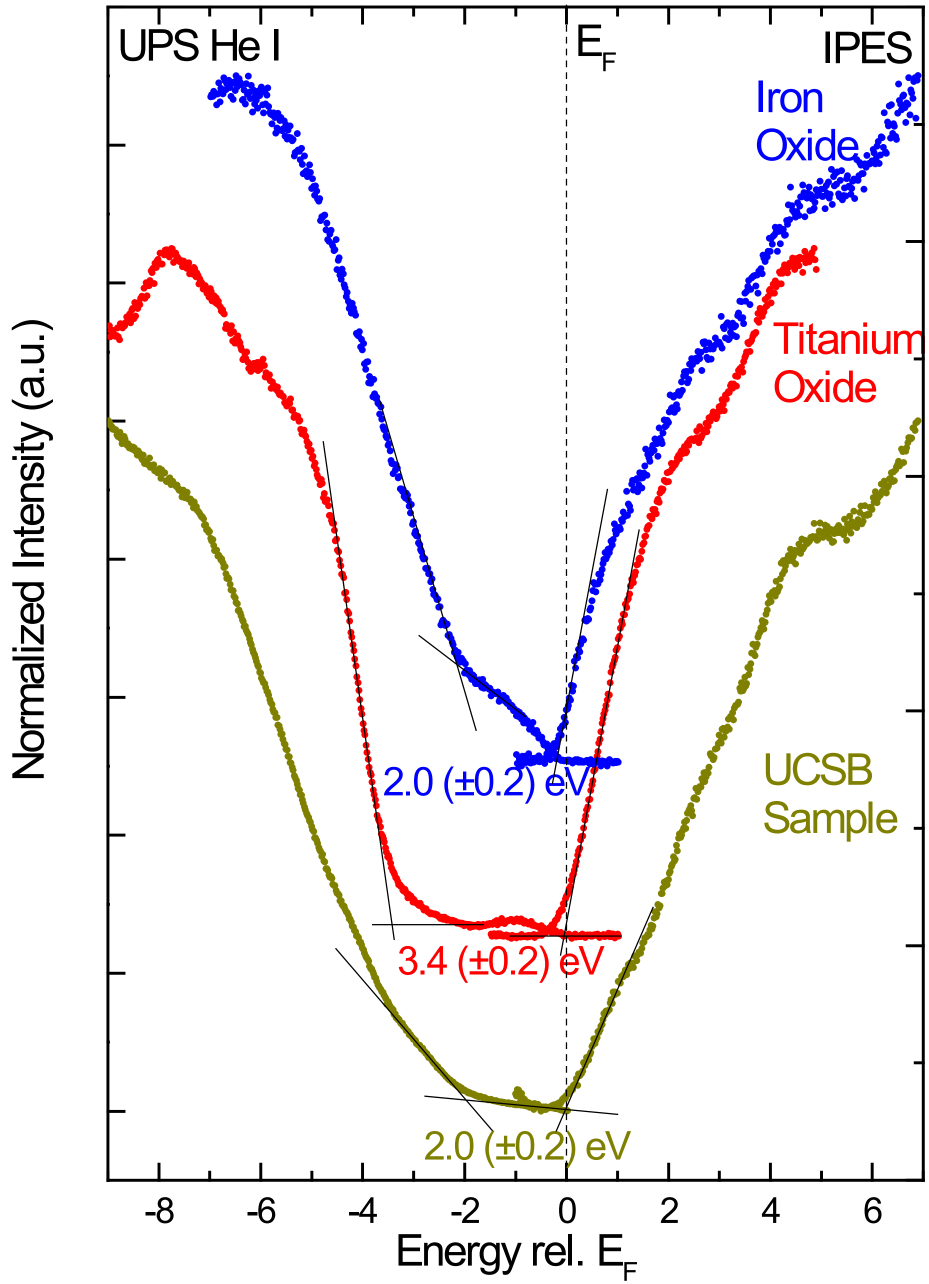
TiO_2

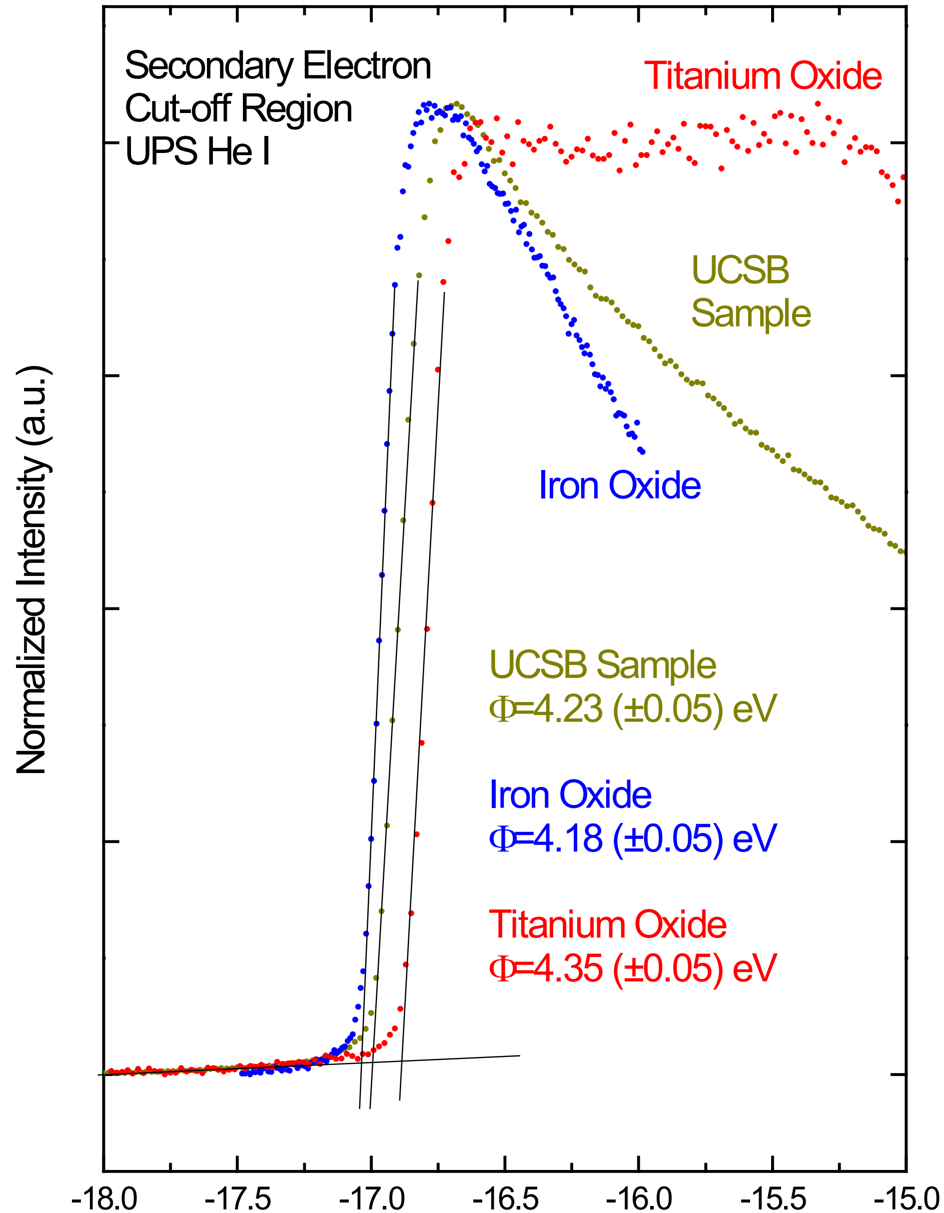
Effect of calcination on thin Fe_2O_3 samples
(FY 2010 Accomplishments)



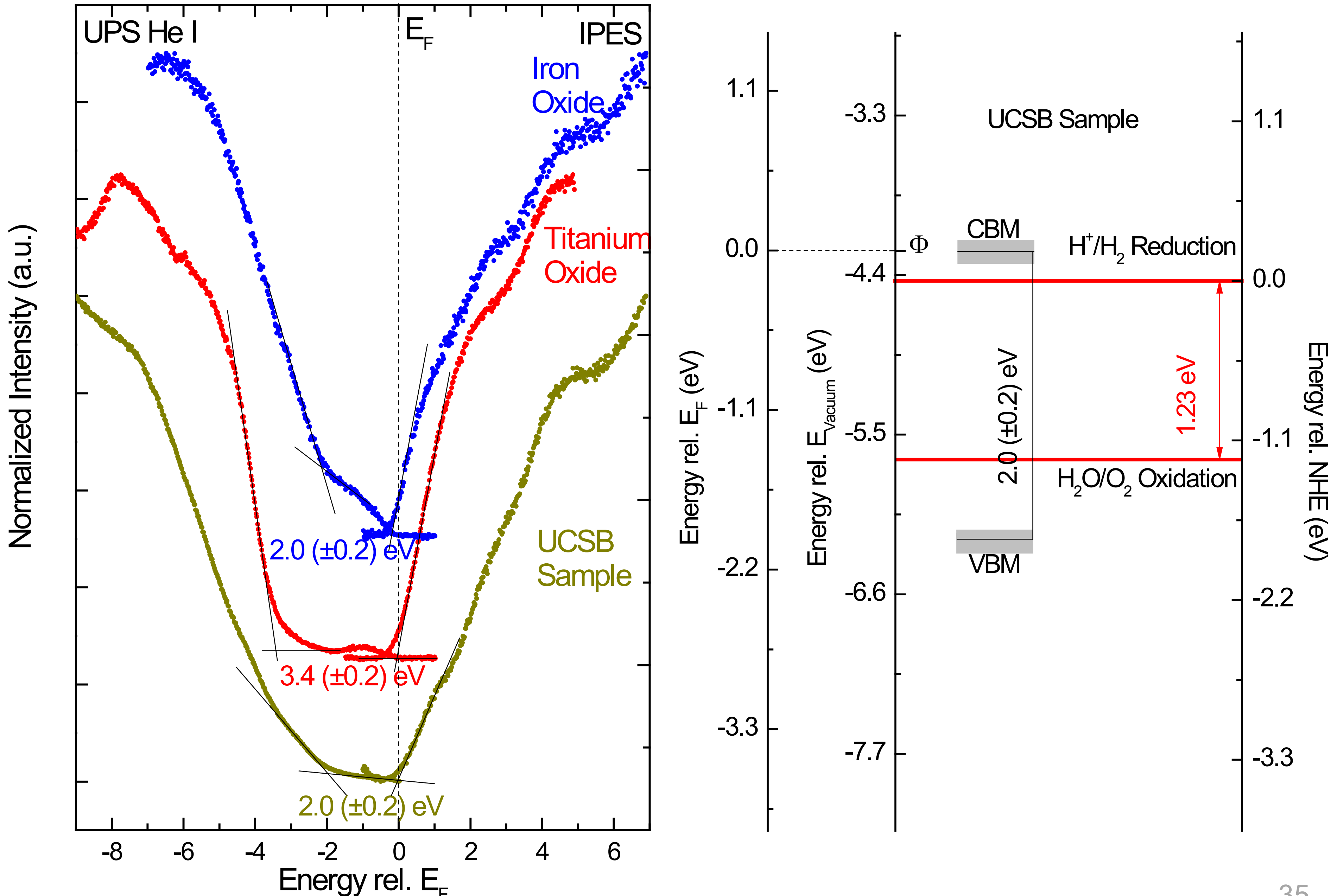
- Ti and Pt are detected at the surface after calcination
- Pt peaks not seen in thicker calcined samples (not shown)

Electronic surface structure (Accomplishments)





Electronic surface structure *(Accomplishments)*



Summary of Fe_2O_3 results
(Accomplishments)

- Earlier findings: calcination modifies chemical surface structure, leading to Ti segregation; in thin films, Pt signals are observed at the surface
- Now: electronic structure at the surface
  - Favorable surface band gap
  - Redox-potentials are straddled, but only barely
- Clarification of “high-performance” character

Research Plan & Basis for Continuation of Research

(Proposed Future Work)

- Continue the collaborations with our existing partners
  - (Ga,In)(P,N) with NREL and LLNL
  - WS_2 and MoS_2 with Stanford
  - WO_3 and $Cu(In,Ga)Se_2$ with HNEI
- 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)
- Depending on funding availability: *in-situ* studies

Overall 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” (*in-situ* on the horizon)
- 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
- Met all program milestones and delivered all deliverables of characterization data and analyses to program collaborators