



Characterization of Materials for Photoelectrochemical Hydrogen Production (PEC)

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May 12, 2011

Project ID #
PD051

Overview

Timeline

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

Budget

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

Barriers

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

Partners

- Interactions/collaborations: DOE EERE PEC WG (NREL, LLNL, HNEI, UCSB, Stanford, MVSsystems), 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**

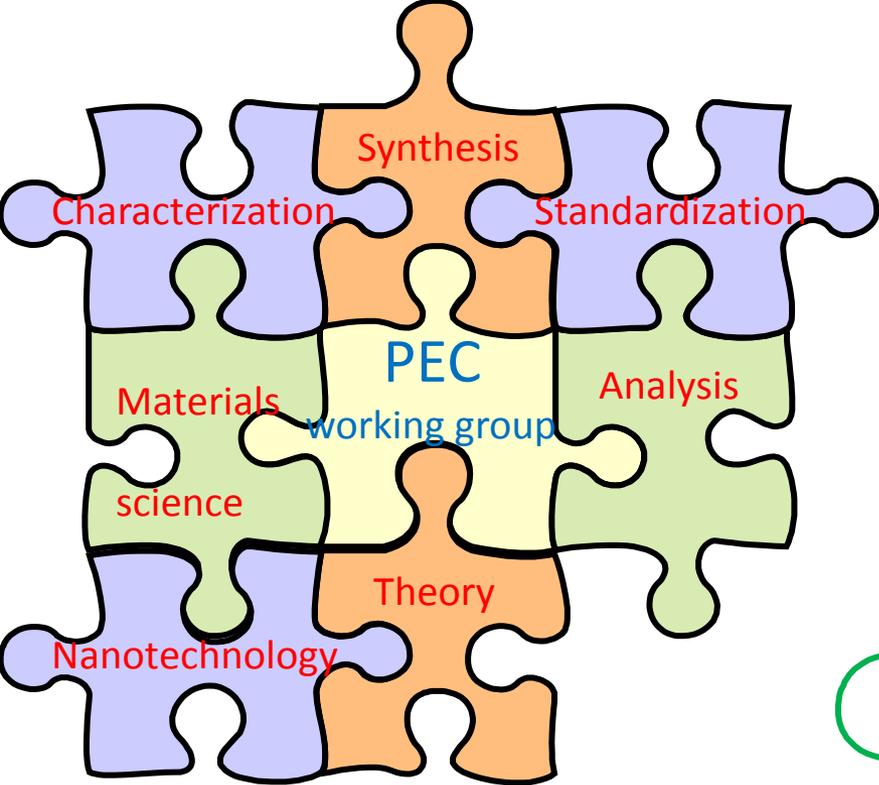
Research Activity (*Approach*)

- **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: $(\text{Ga,In})\text{P}_2$
 - UC Santa Barbara: Fe_2O_3 et al.
 - Stanford U: MoS_2
 - LLNL: Theory ($(\text{Ga,In})\text{P}_2$, liquid/solid interfaces)
 - U Hawaii/HNEI: WO_3 , $\text{W}(\text{X})\text{O}(\text{Y})_3$, $\text{Cu}(\text{In,Ga})(\text{S,Se})_2$

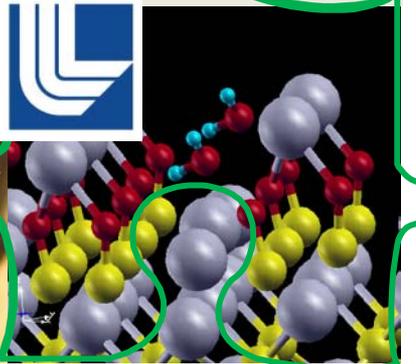
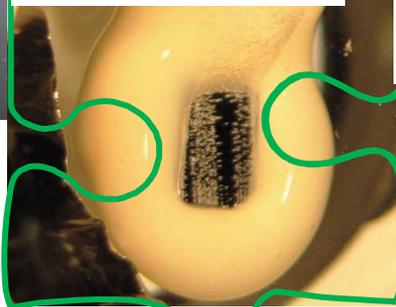
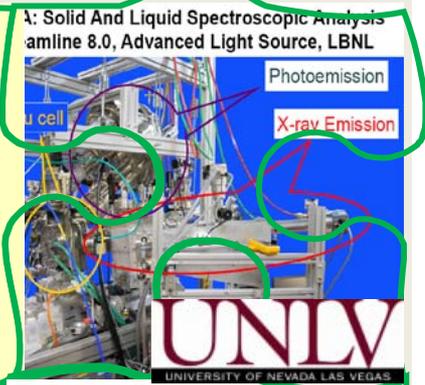
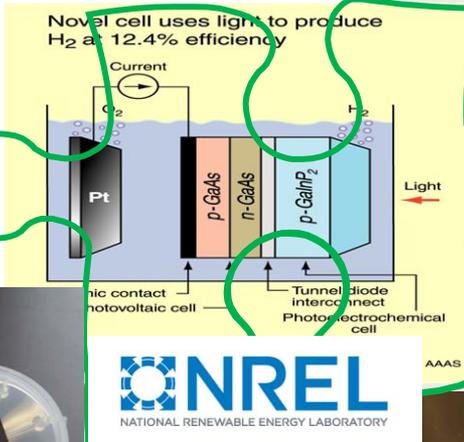


PEC Working Group:
 Evaluating working directions
 Sharing and building-up knowledge
 Accelerating research progress

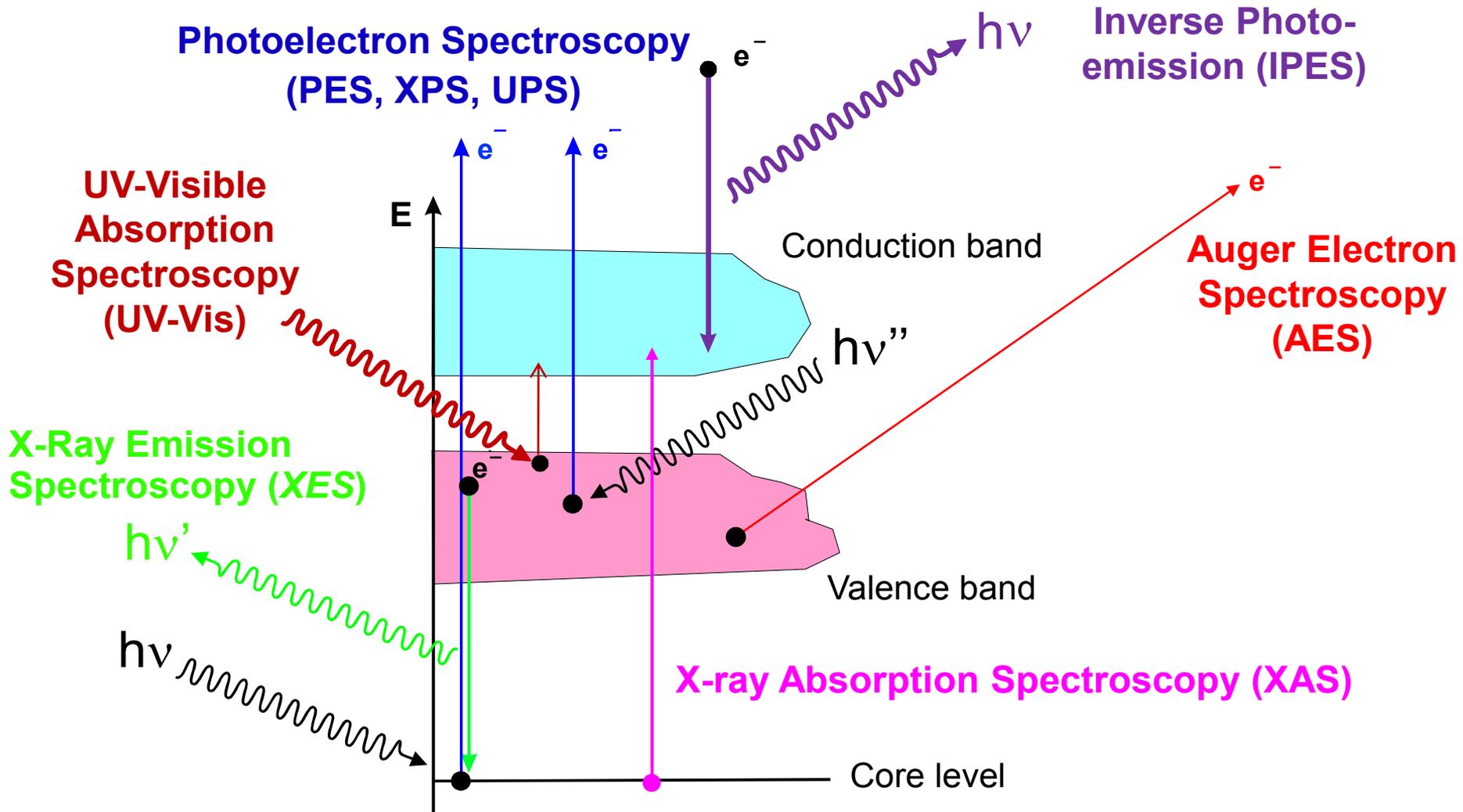
- **Advanced Characterization Support : III-V, Sulfides, Oxides**
- **III-V Surface Validation**



DOE Targets: >1000h @STH > 8% (2013)
 \$2 - 4/kg H₂ projected PEC cost
 (beating >\$10/kg H₂ for PV-electrolysis)



UV/Soft X-ray Spectroscopies (Approach)

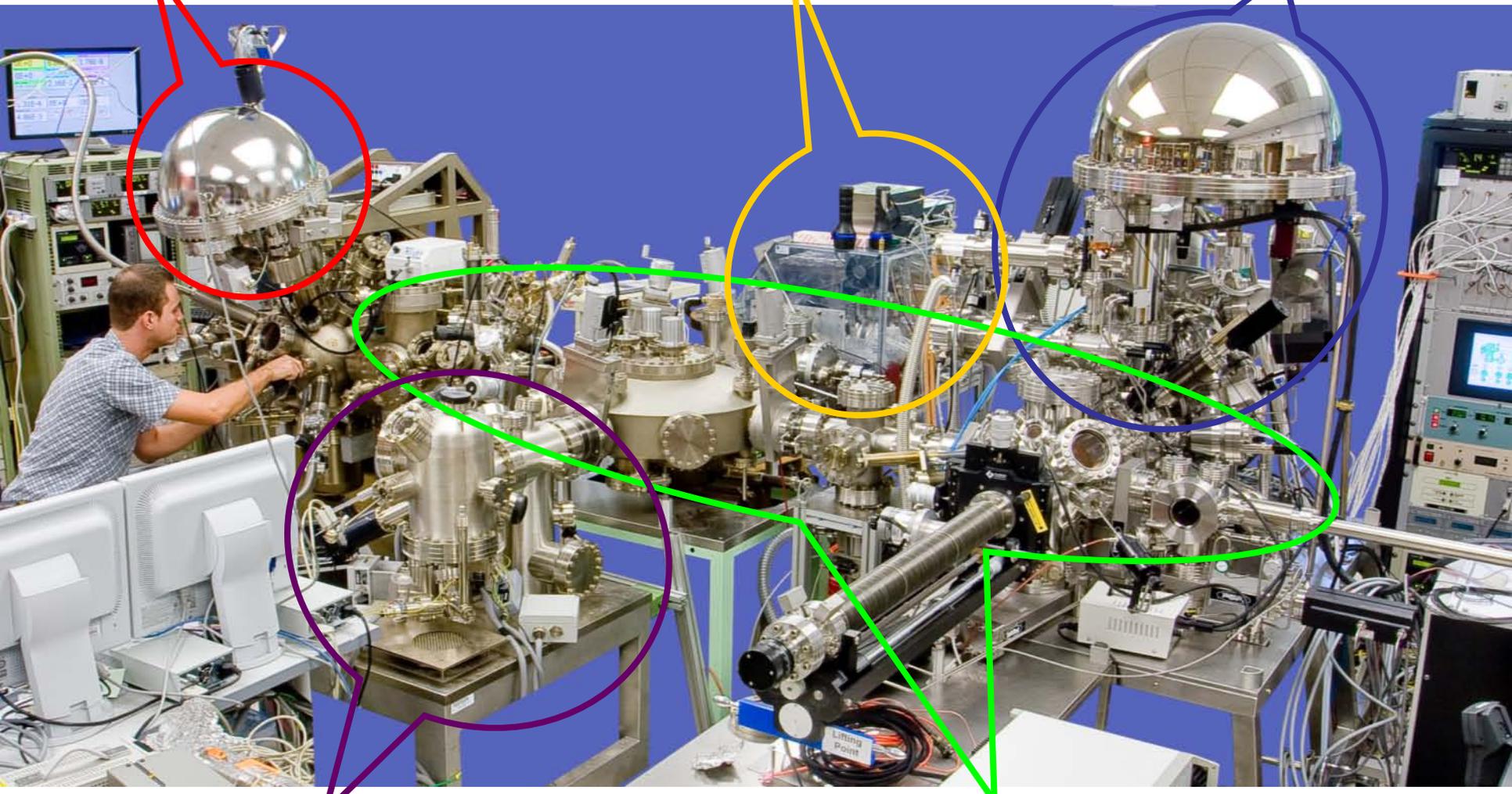


Plus: Atomic Force Microscopy ₇

High dynamic range
XPS, UPS, Auger, IPES

Glovebox

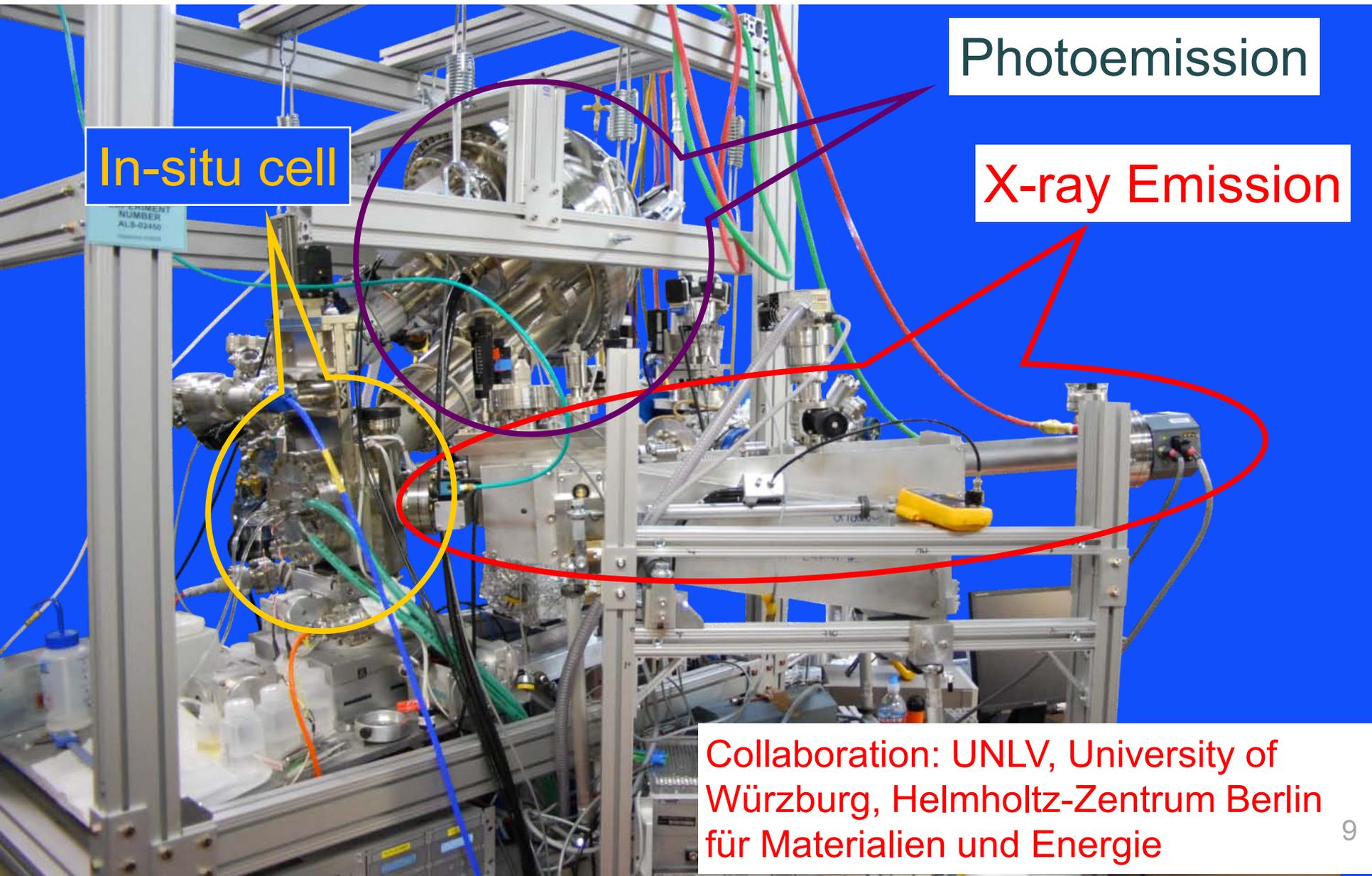
High resolution
XPS, UPS, Auger



Scanning Probe
Microscope

Sample preparation
and distribution

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



In-situ cell

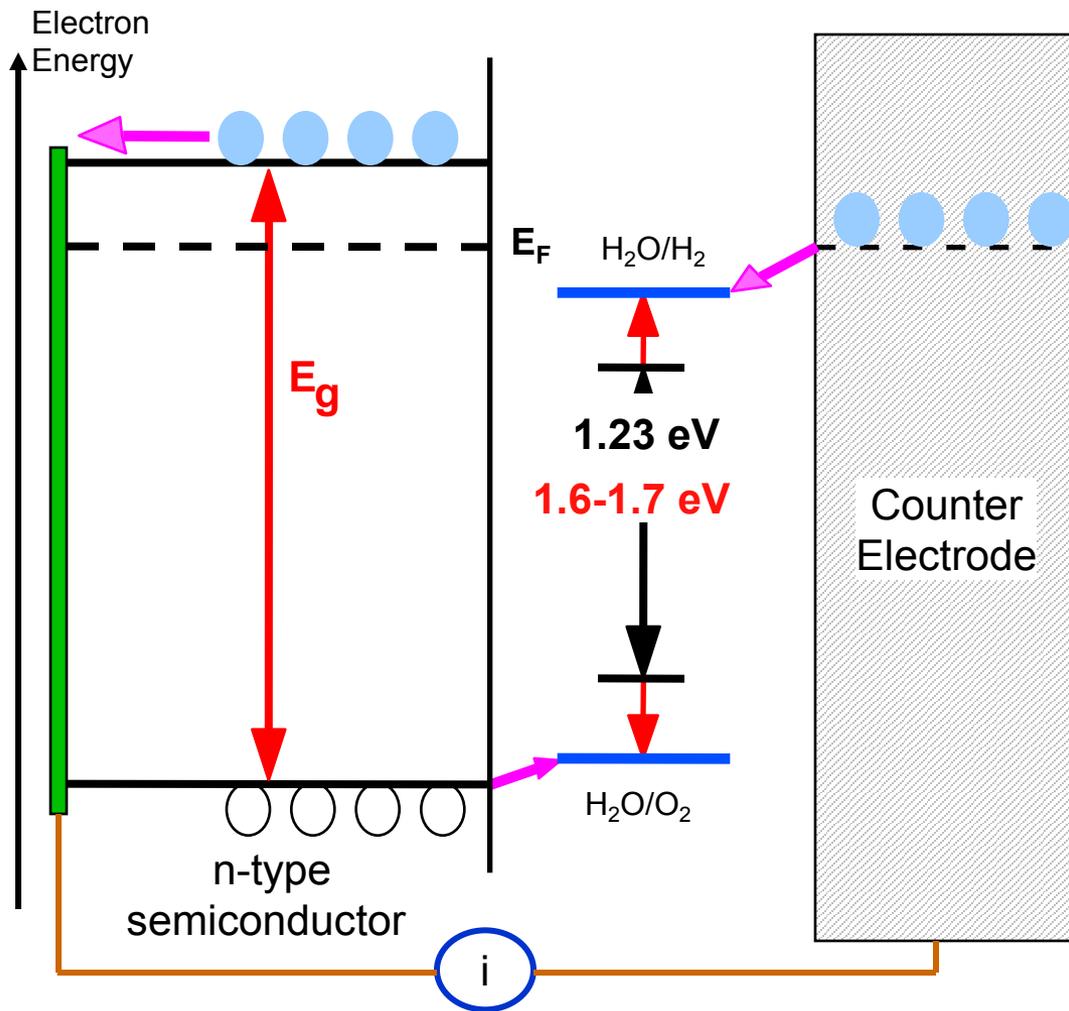
Photoemission

X-ray Emission

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 H₂O redox potentials

All must be satisfied
simultaneously

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

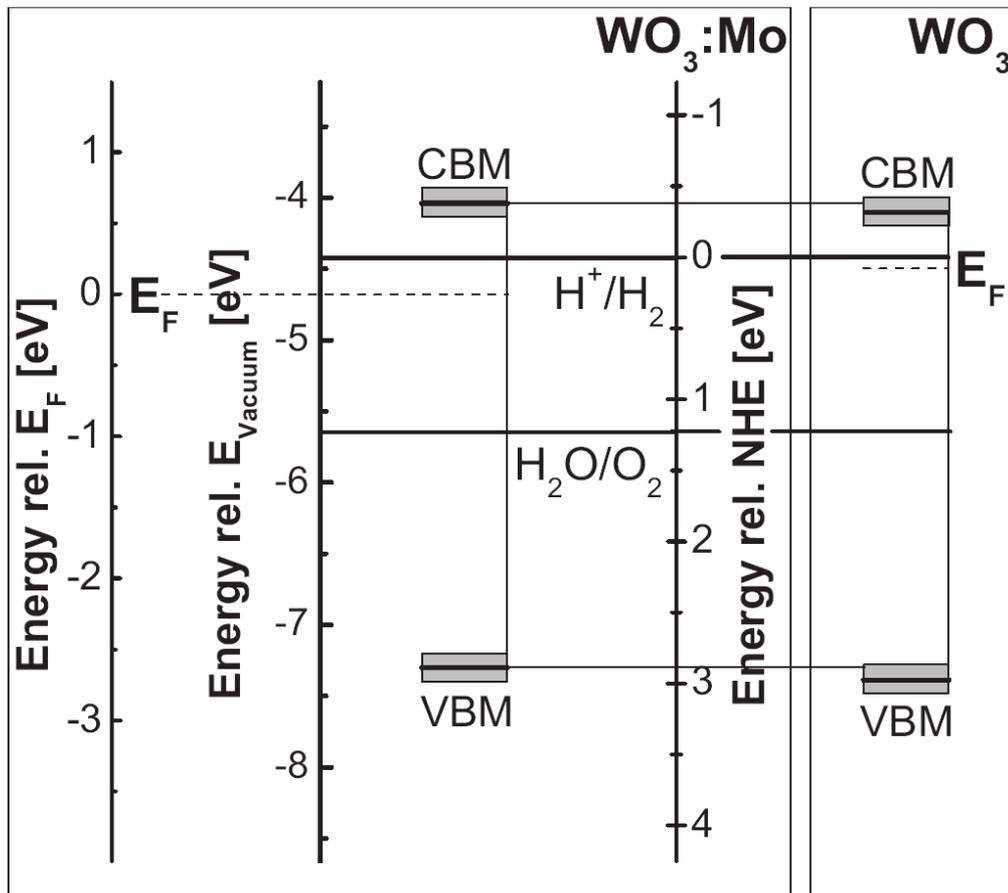
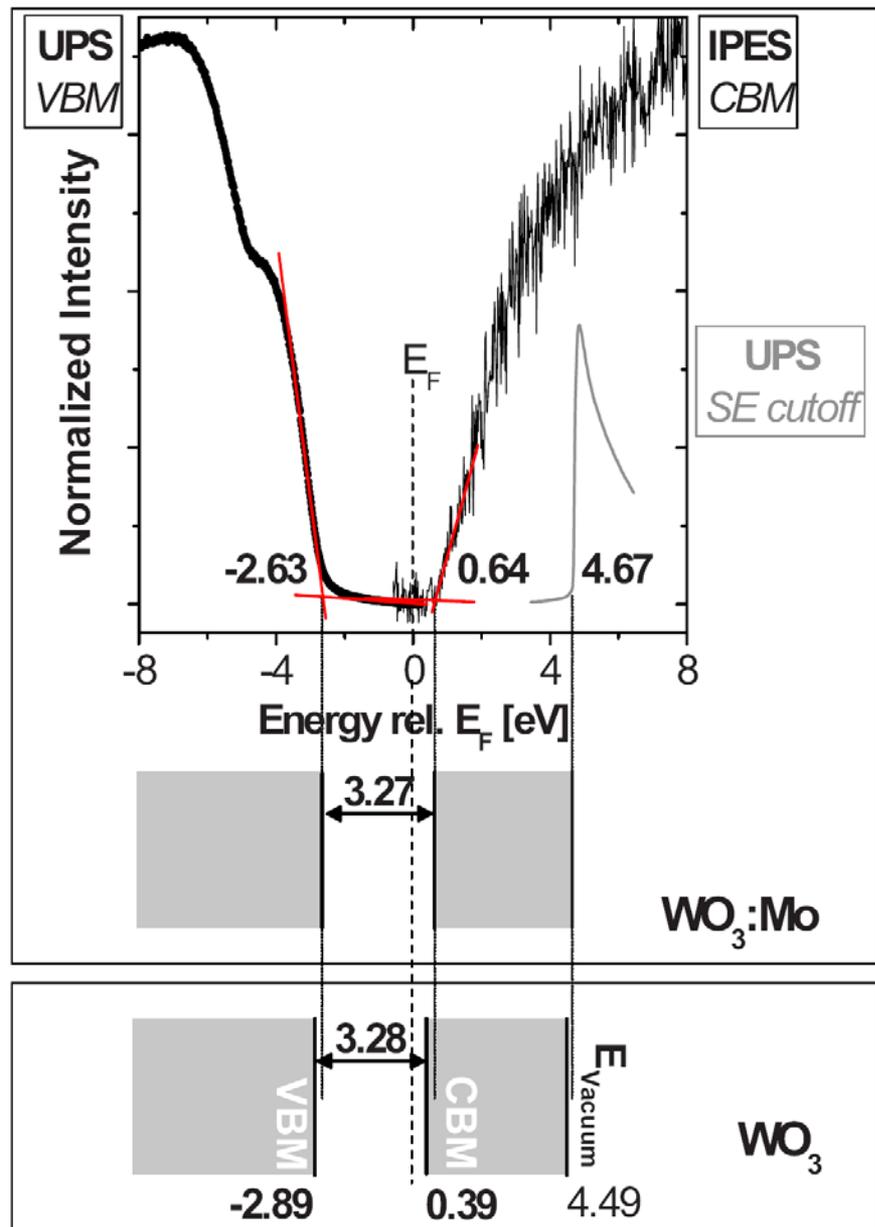
David Prendergast
Lawrence Berkeley National Laboratory



For more details, please see PD035 and PD058

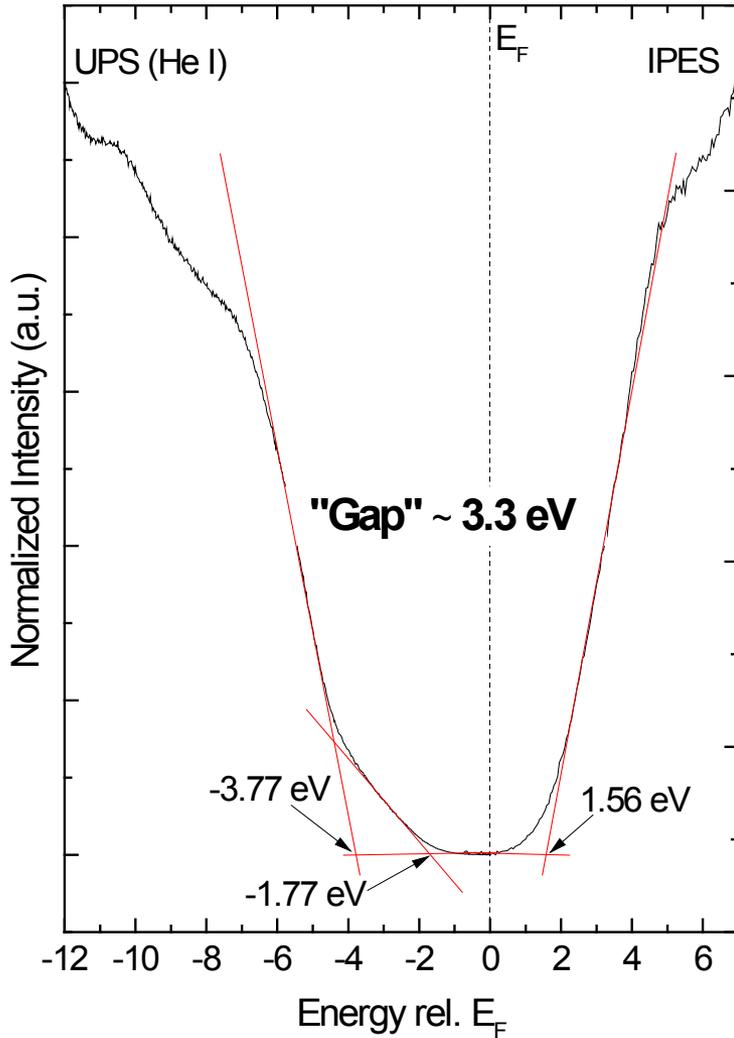
Motivation: compile data for $(\text{Ga,In})_x\text{P}_y$ similar to previous results on WO_3 and $\text{WO}_3:\text{Mo}$

(FY 2010 Accomplishments)

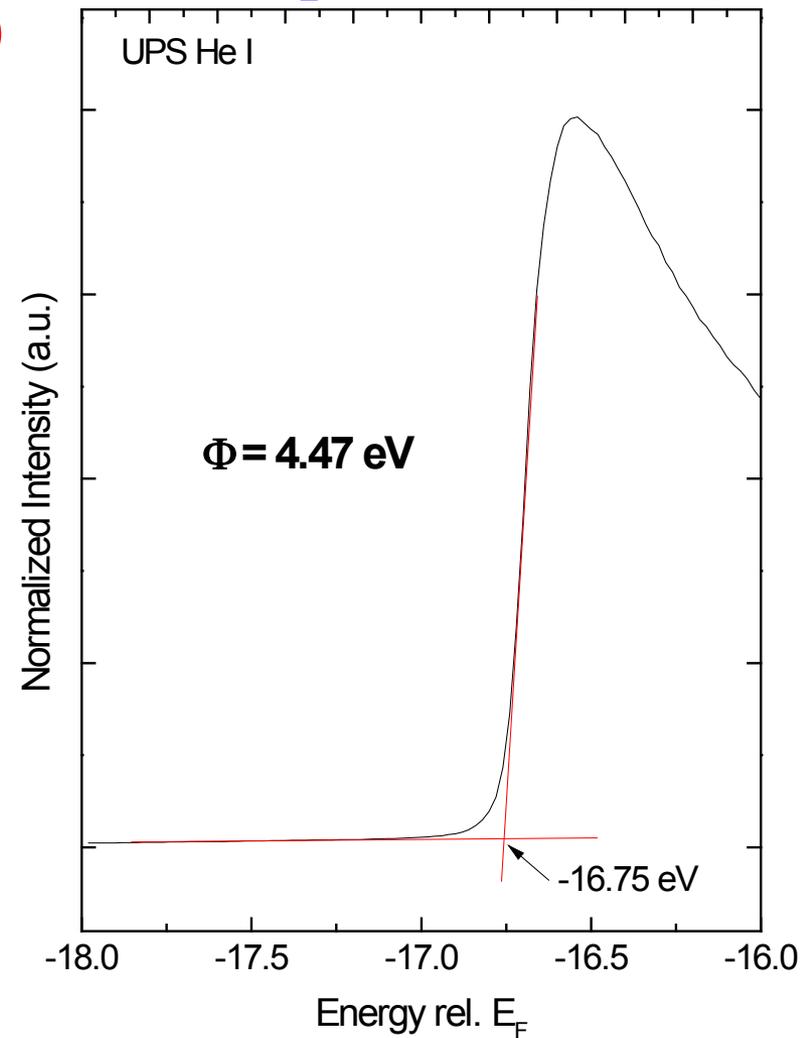


APL 96, 032107 (2010)

Electronic surface structure of as-received GaInP_2 surface ("dirty")



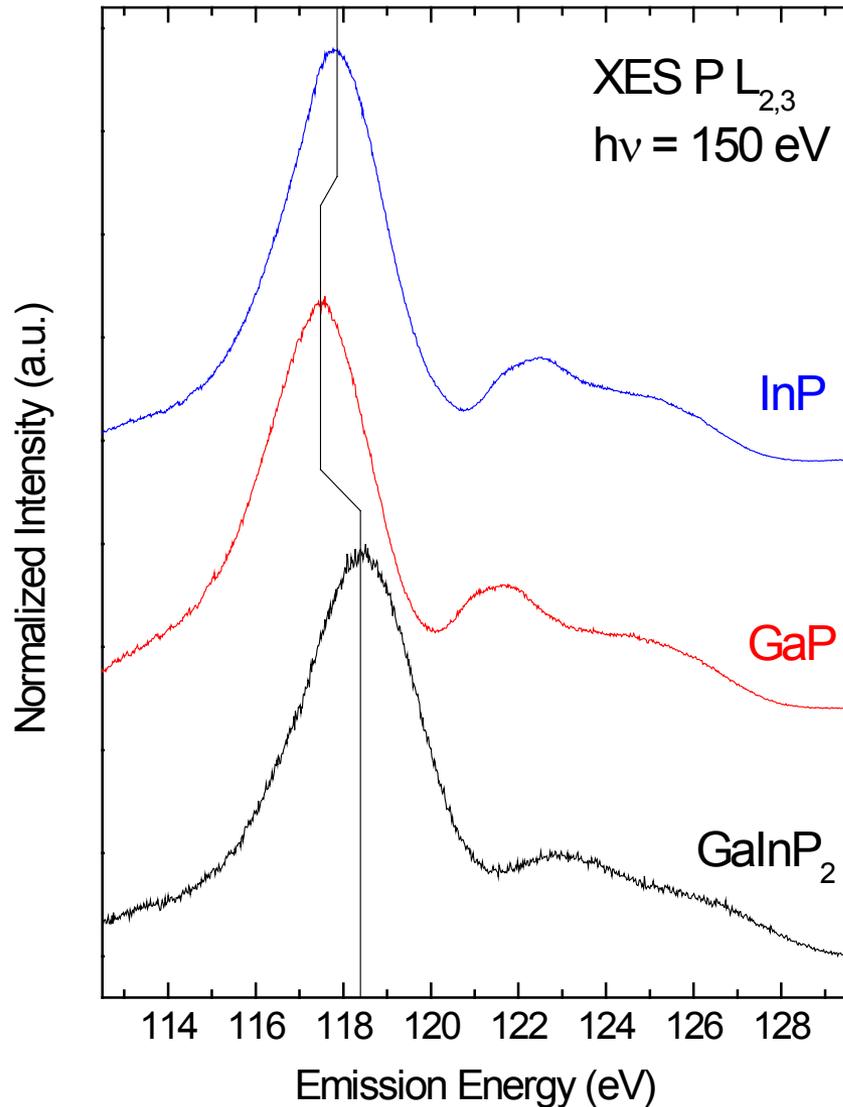
(Accompl.)



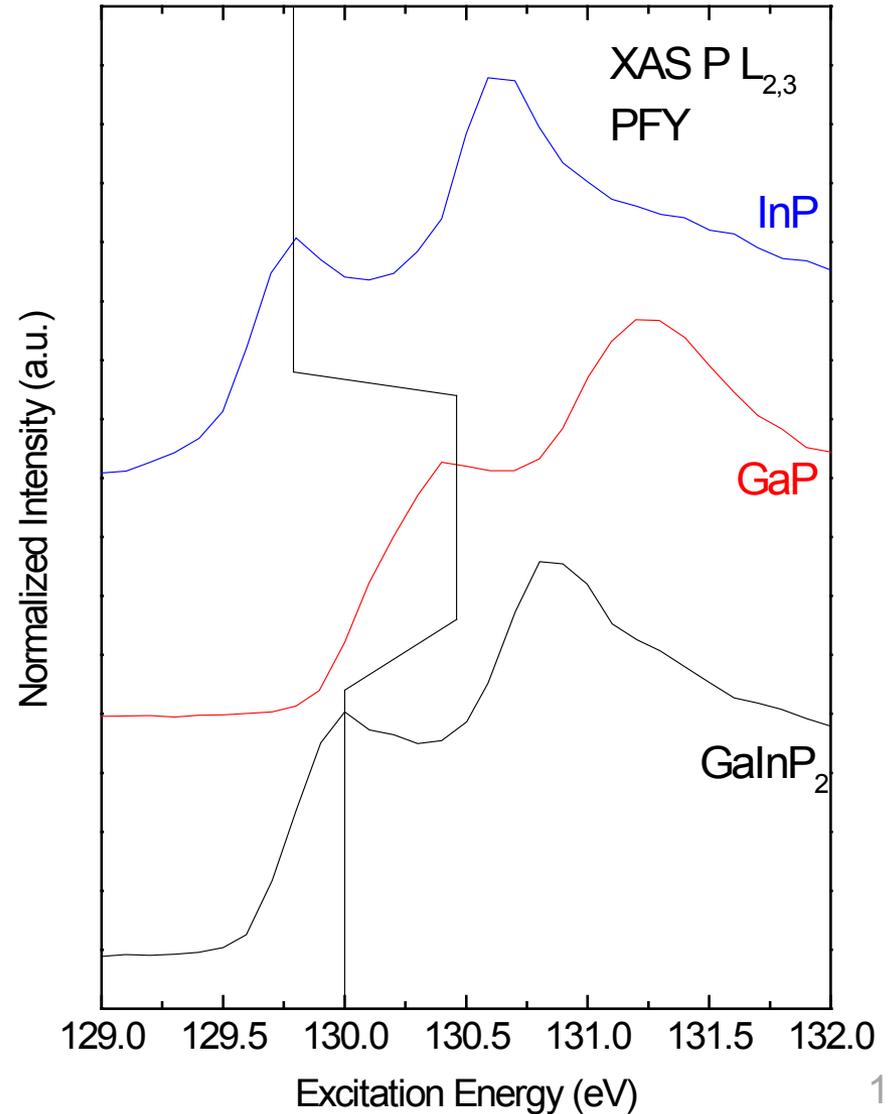
- Surface-sensitive measurements are powerful, but are also influenced by surface adsorbates
- HOMO-LUMO energy separation of surface adsorbates ("band gap"): ~ 3.3 eV
- Compare: UV-Vis and photocurrent spectroscopy (NREL): ~ 1.8 eV
- Work function of surface adsorbates: ~ 4.5 eV
- Current work: optimize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

XES & XAS of InP, GaP, and GaInP₂ *(Accomplishments)*

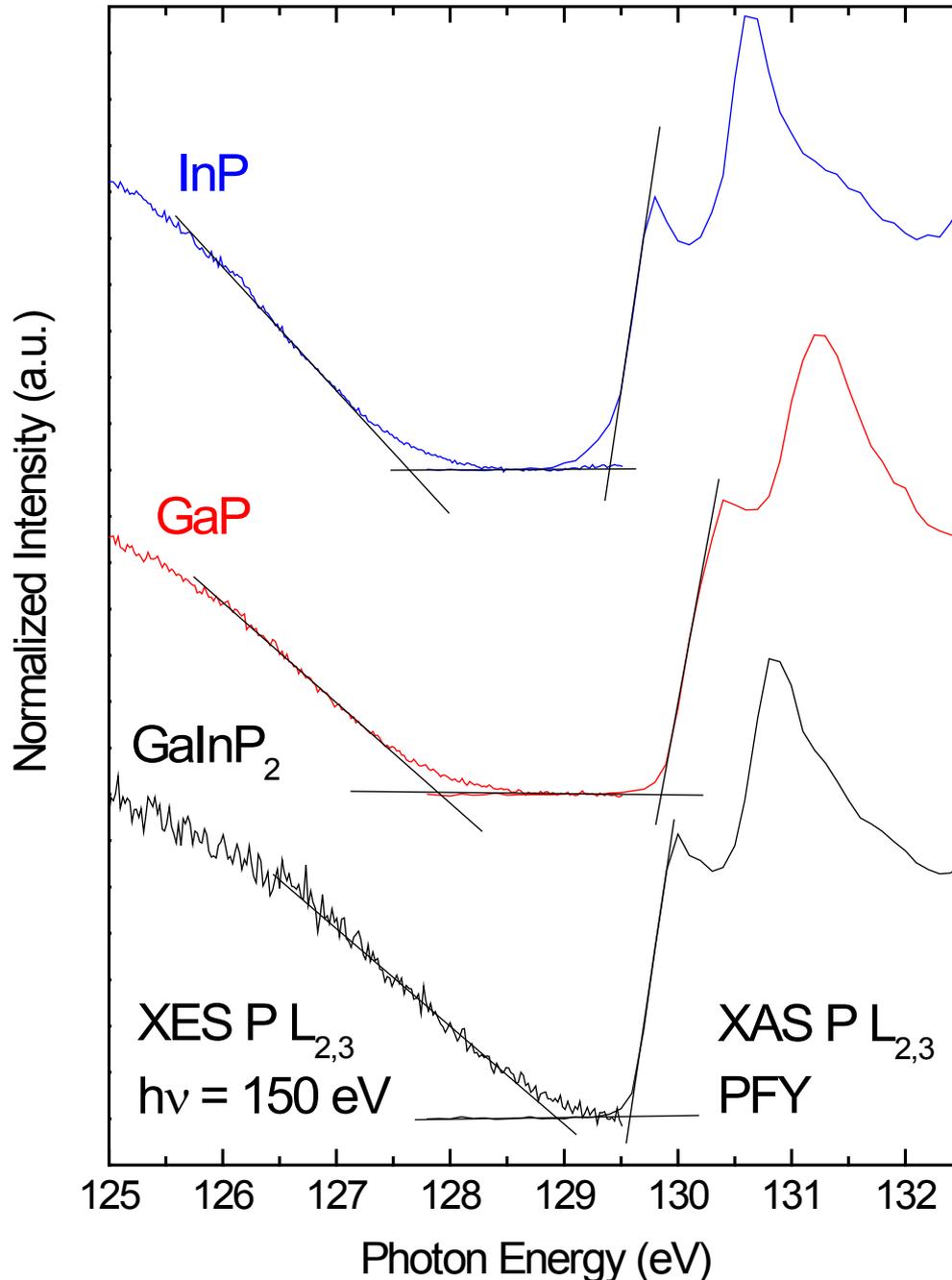
Occupied electronic states



Unoccupied electronic states

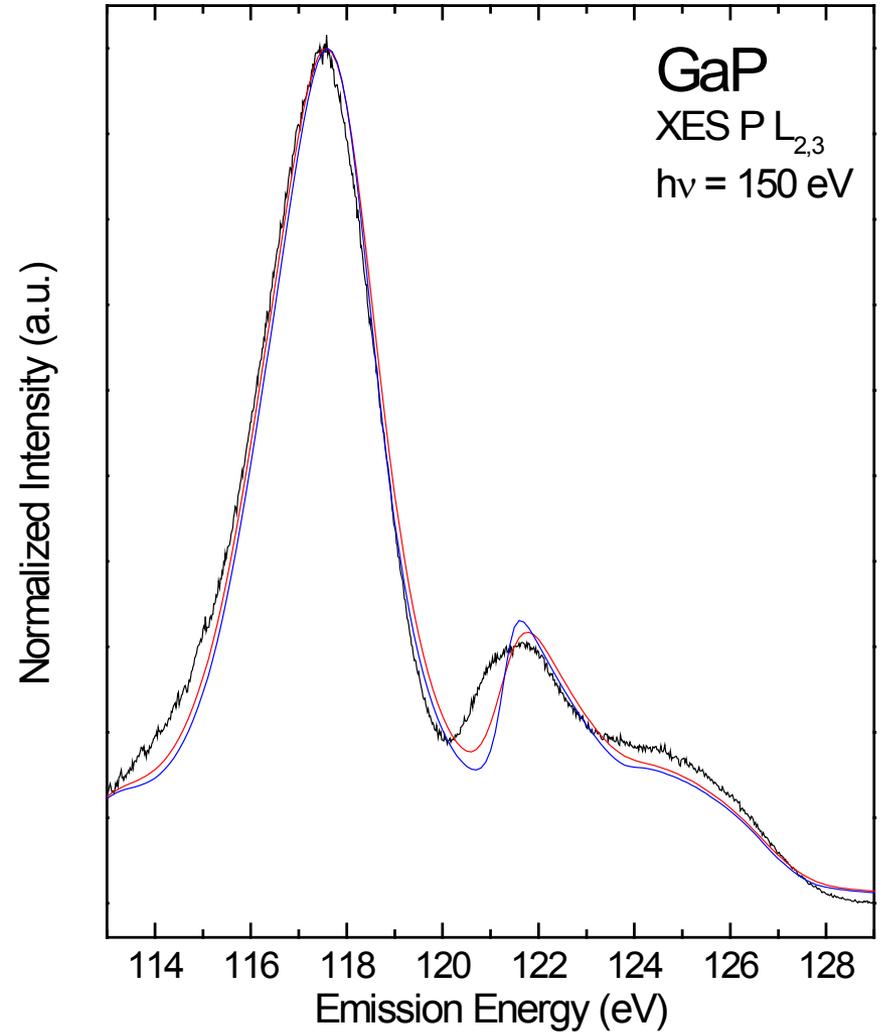
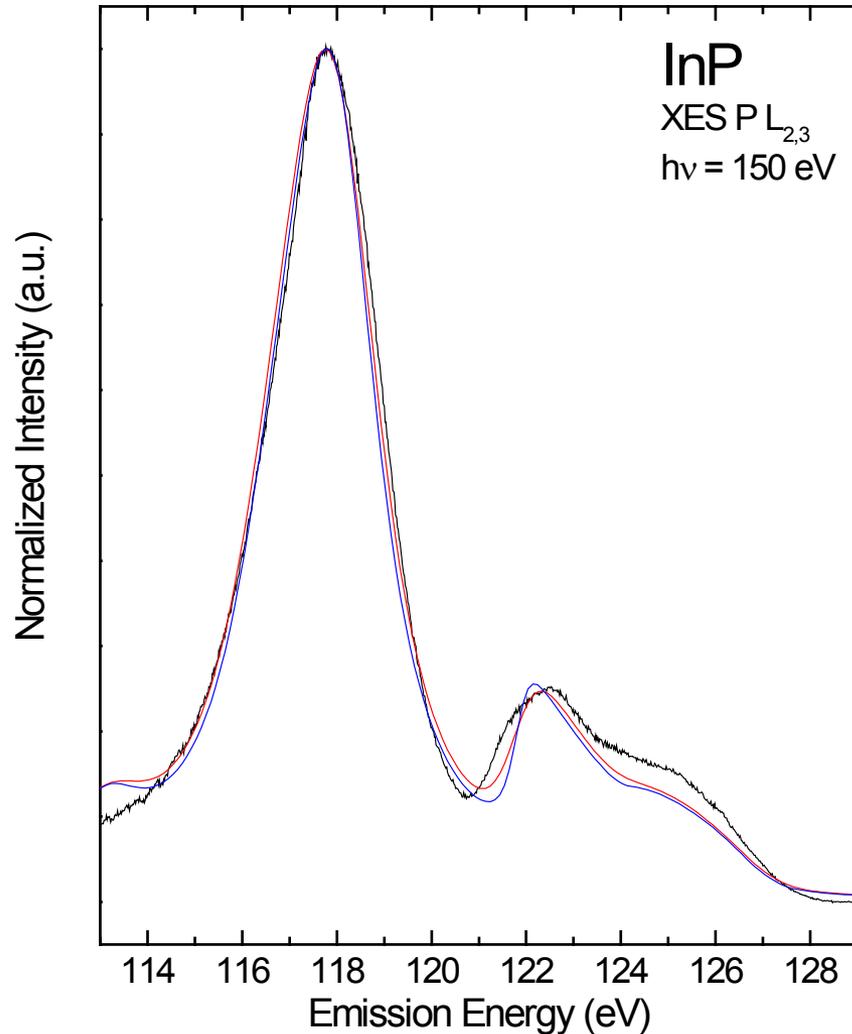


XES & XAS of InP, GaP, and GaInP₂ (Accomplishments)



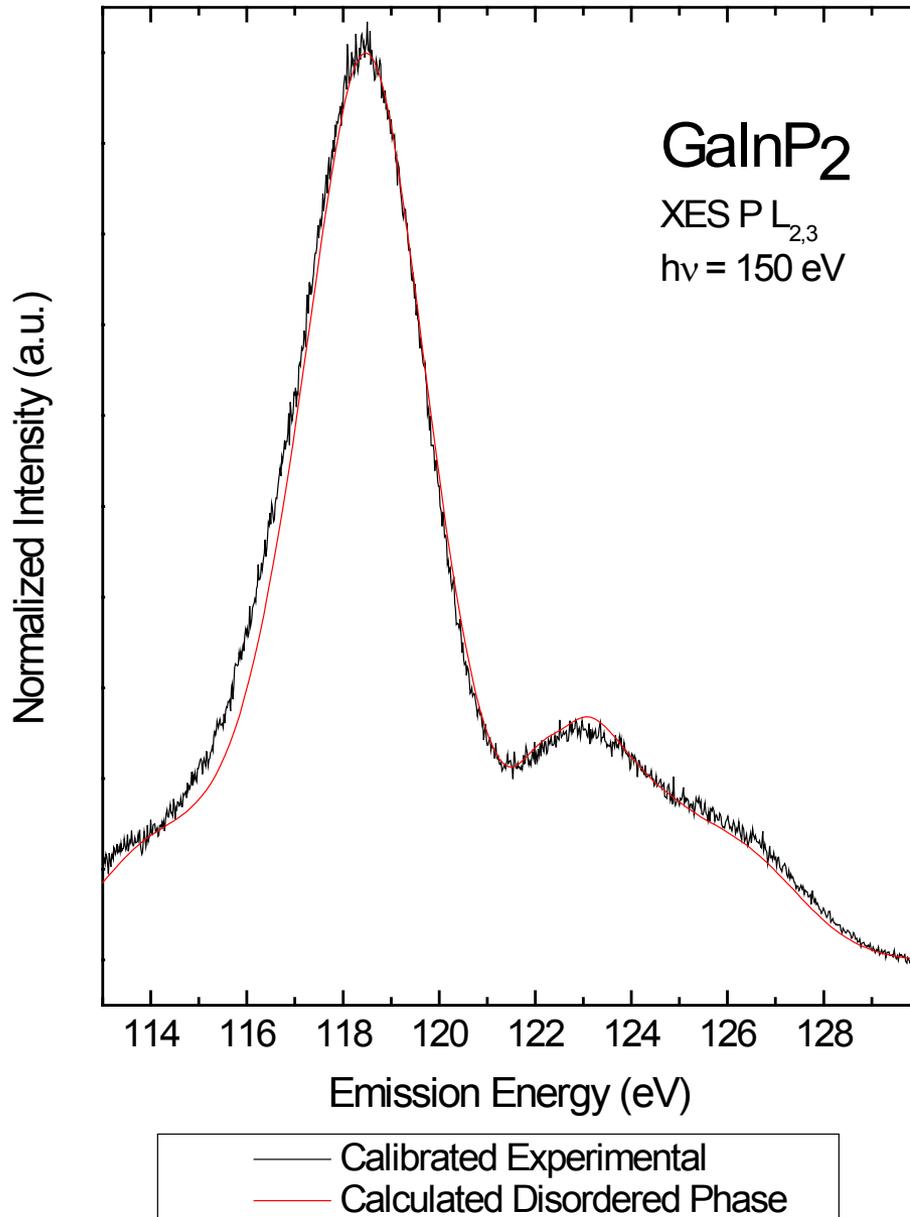
- Lower bound for electronic surface-near bulk band gap can be determined
 - Needs to take core-exciton and spin-orbit splitting (0.84 eV) into account
- Derived lower-bound band gaps:
 - InP: 2.6 eV (Lit: 1.34 eV)
 - GaP: 2.8 eV (Lit: 2.46 eV)
 - GaInP₂: 1.5 eV (1.75 eV)
- Needs theory (and cleaner samples) for better understanding

XES: Comparison of Theory and Experiment (*Accompl.*)



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

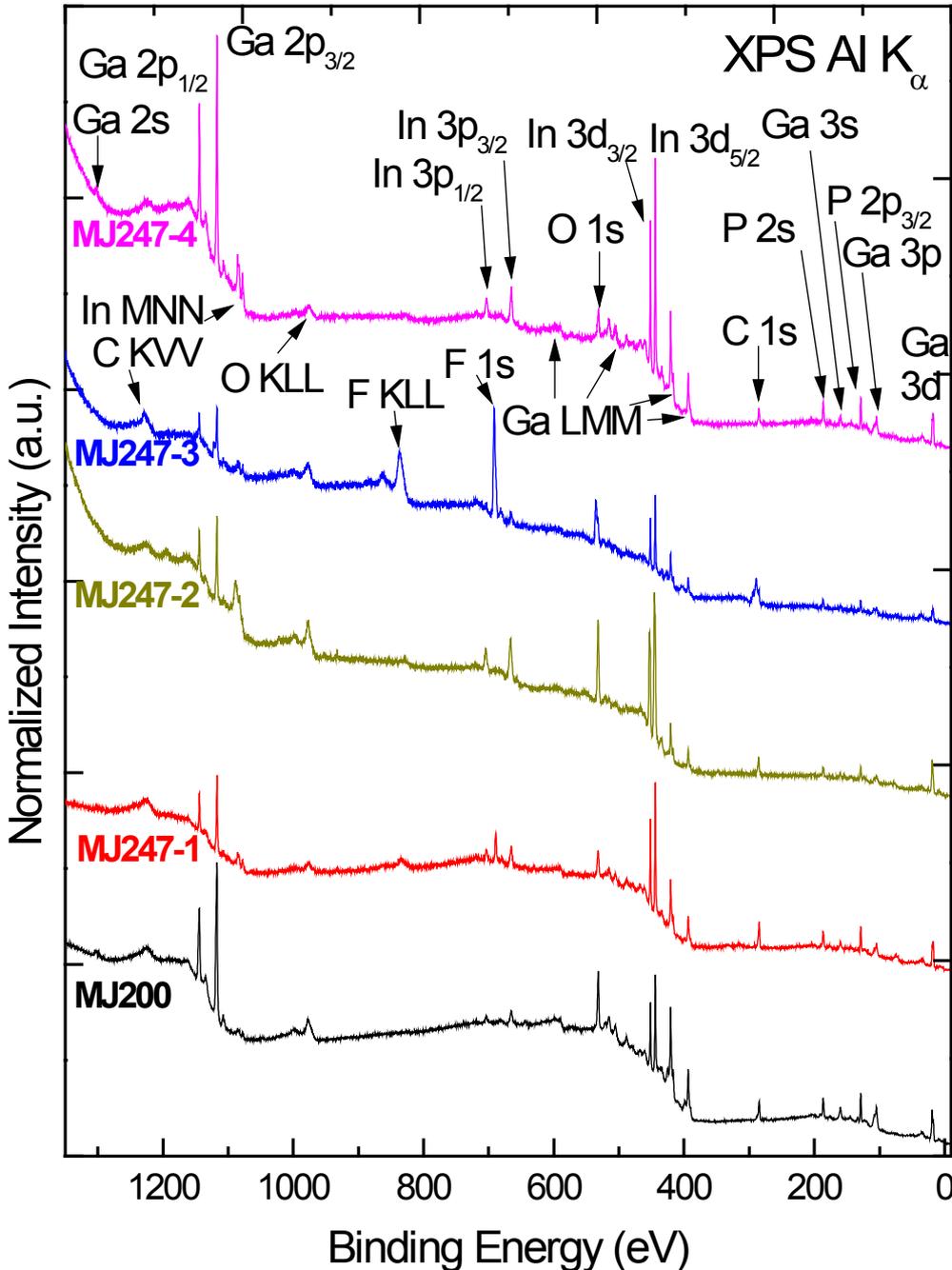
XES: Comparison of Theory and Experiment (*Accompl.*)



- Excellent agreement between theory and experiment for all three compounds (InP, GaP, GaInP₂)
- 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 $_4$ NO $_3$ w/ Zonyl $^{\text{®}}$ FSN-100
MJ247-2	-8mA/cm 2 , 22hrs, AM1.5G	1M KOH w/ Zonyl $^{\text{®}}$ FSN-100
MJ247-1	-8mA/cm 2 , 22hrs, AM1.5G (+8mA/cm 2 applied for ~1 sec prior to run)	0.5M H $_2$ SO $_4$ w/ Zonyl $^{\text{®}}$ FSN-100
MJ200	as-grown	

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

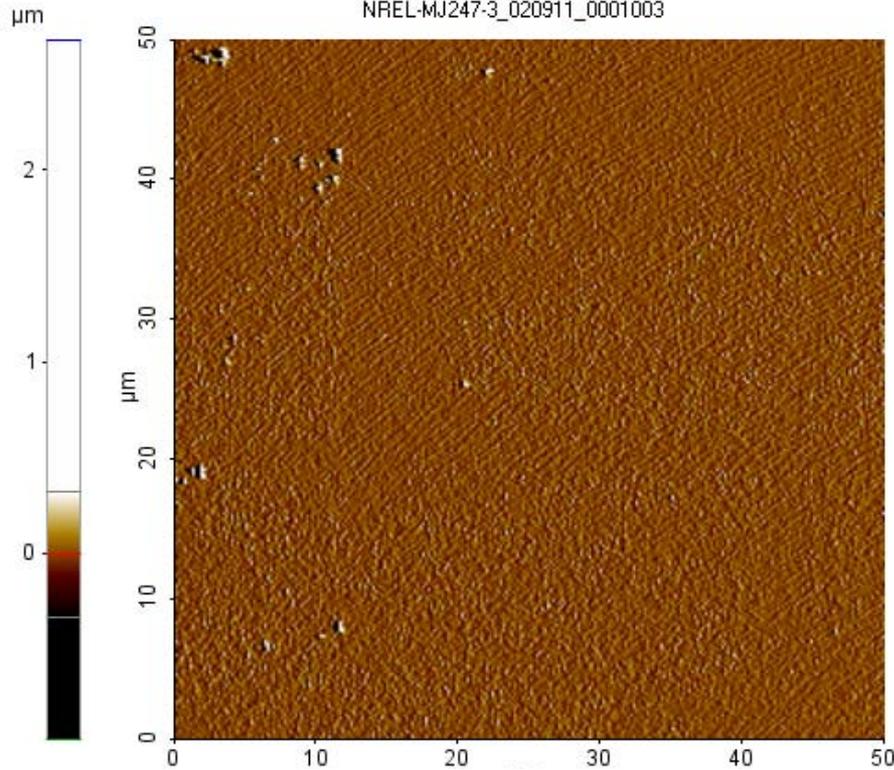
Sample	Treatment	Electrolyte
MJ247-3	-8mA/cm ² , 22 hrs, AM1.5G	0.1M HNO ₃ +0.5M NH ₄ NO ₃ w/ Zonyl FSN-100



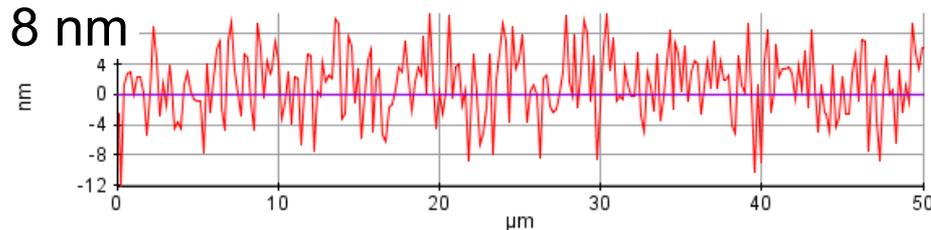
Impact of Exposure to Electrolyte (*Accomplishments*)

Unexposed Region

NREL-MJ247-3_020911_0001003

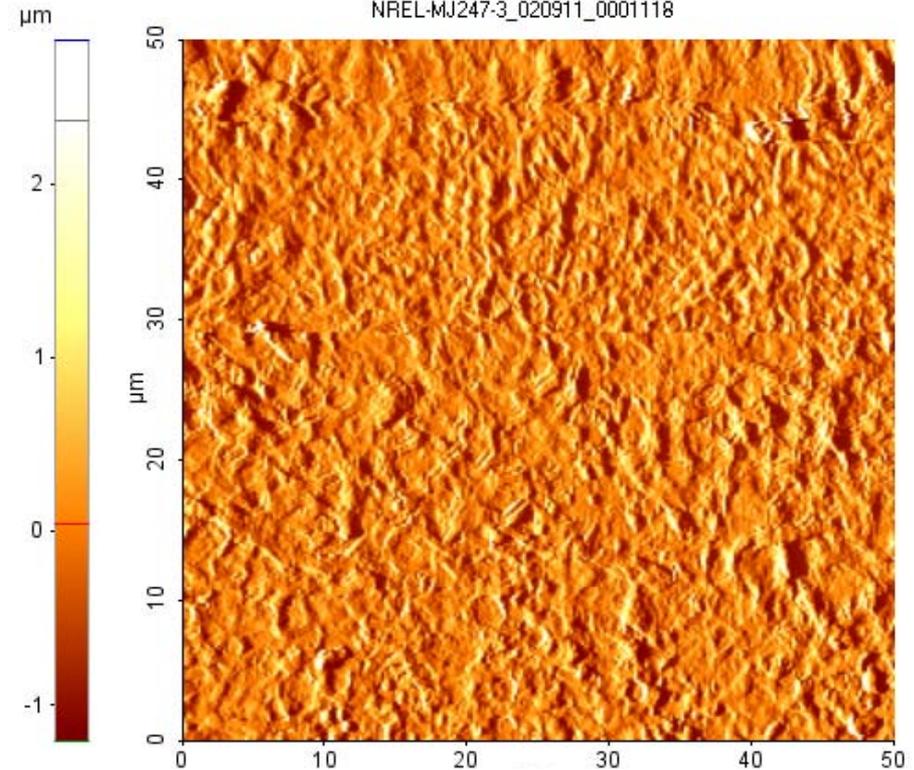


Line Profile: Red

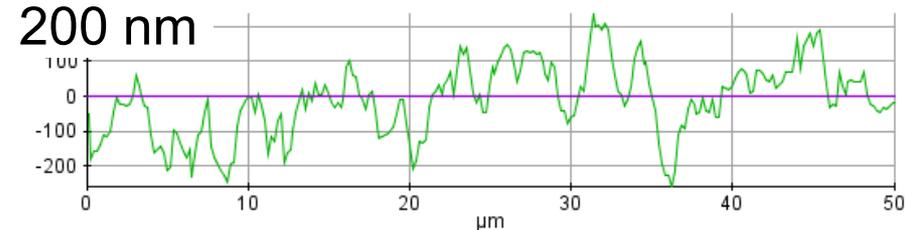


Exposed Region

NREL-MJ247-3_020911_0001118

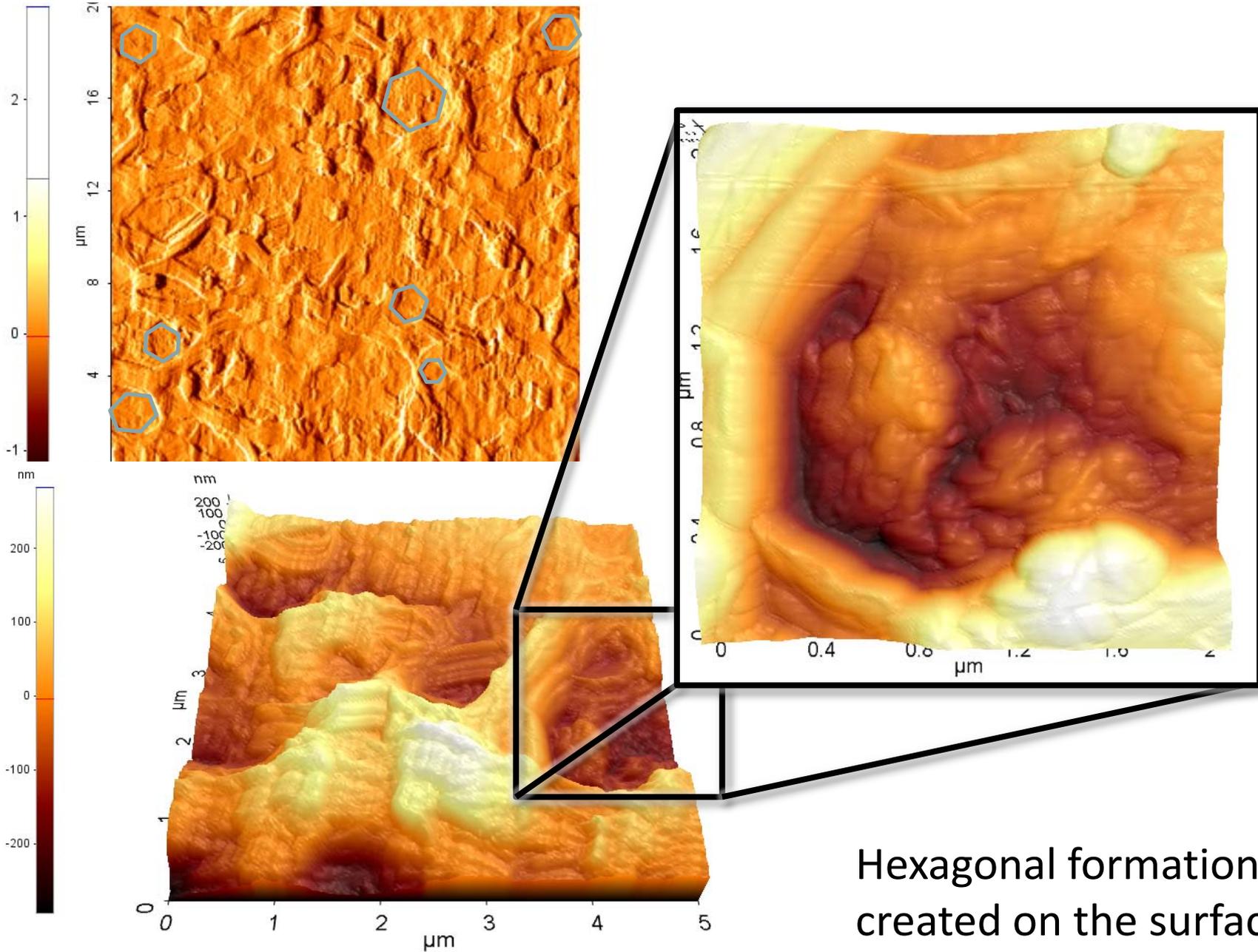


Profile: Green



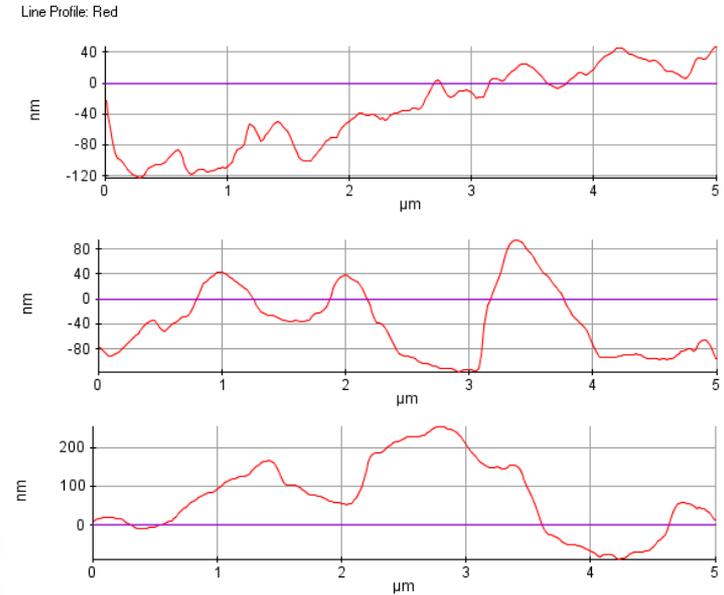
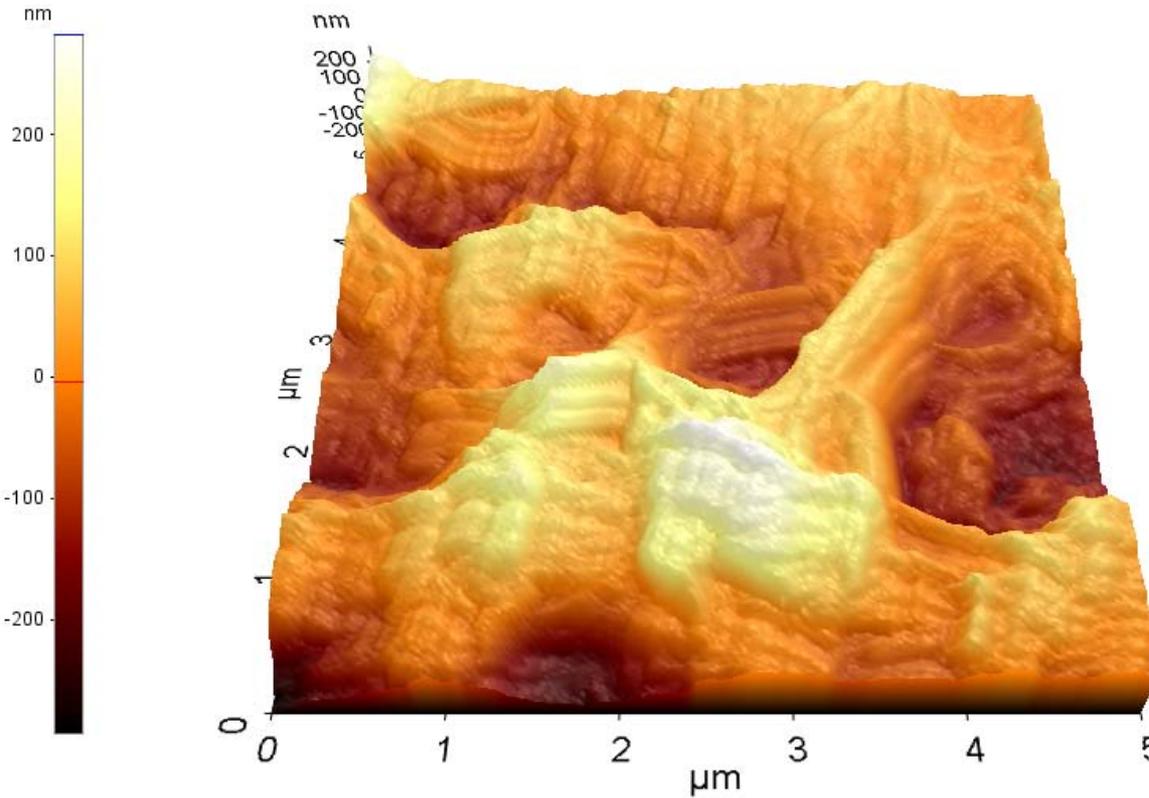
- The region of the sample exposed to electrolyte exhibits surface roughness not seen in the unexposed region
- The exposed region is highly corrugated, whereas the unexposed region is flat and appears ordered

Impact of Exposure to Electrolyte (*Accomplishments*)

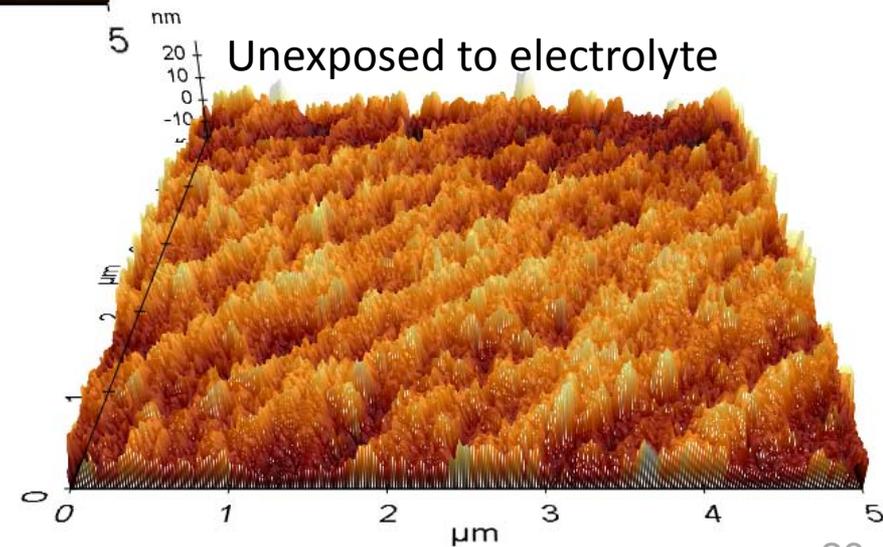


Hexagonal formations are created on the surface

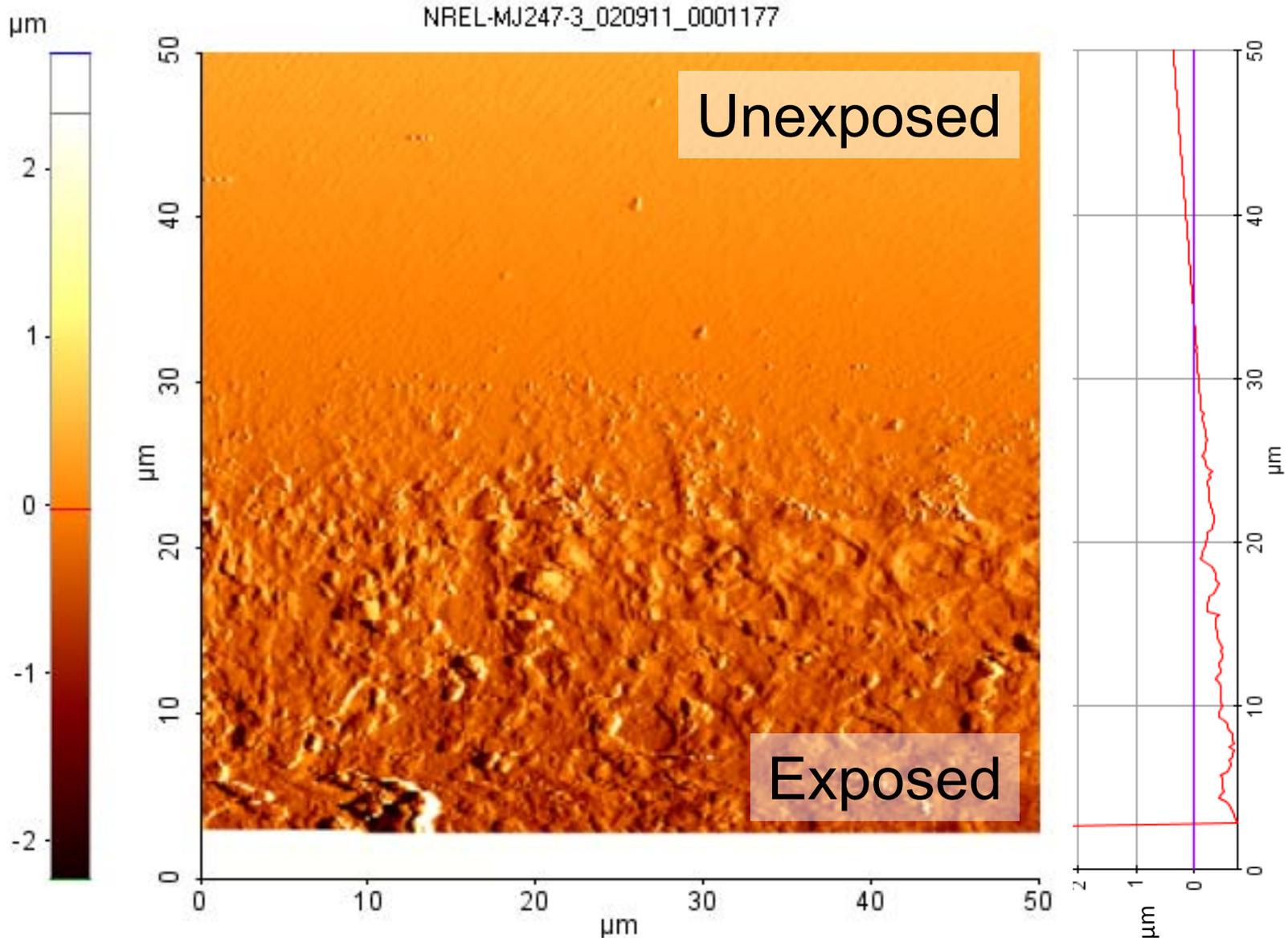
Comparison: Before/After Exposure (Accomplishments)



- 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 excellent agreement
- First analysis of electrolyte exposure
 - Chemical changes (XPS)
 - Morphological changes (AFM)
 - Future: spectroscopy *in-situ* (XES/XAS)

MoS₂ nanomaterials for PEC

With:

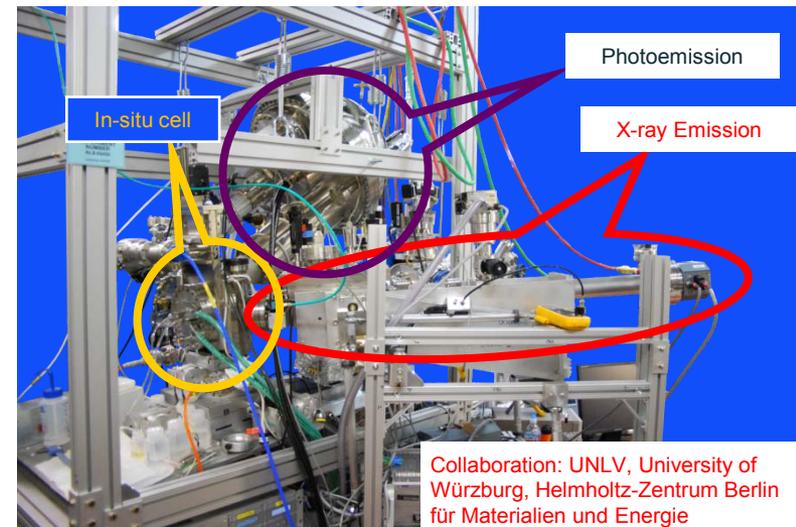
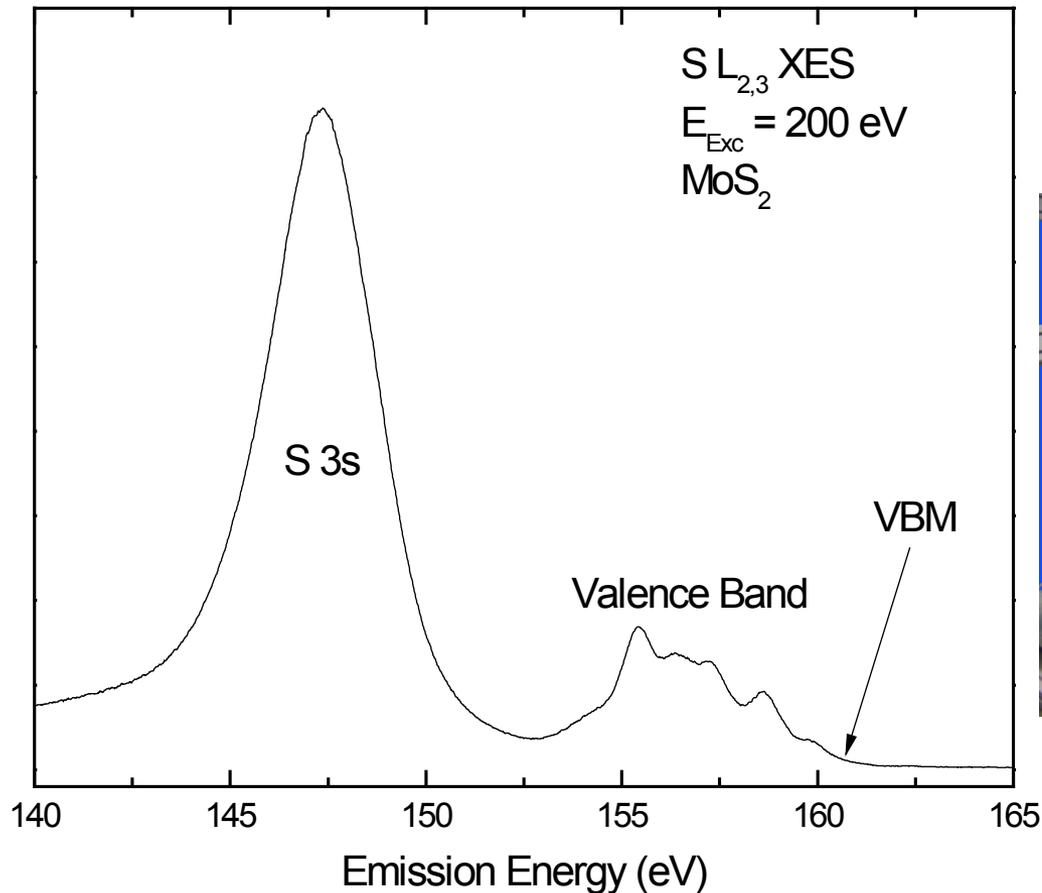
Zhebo Chen and Tom Jaramillo
Stanford University



For more details, please see PD033

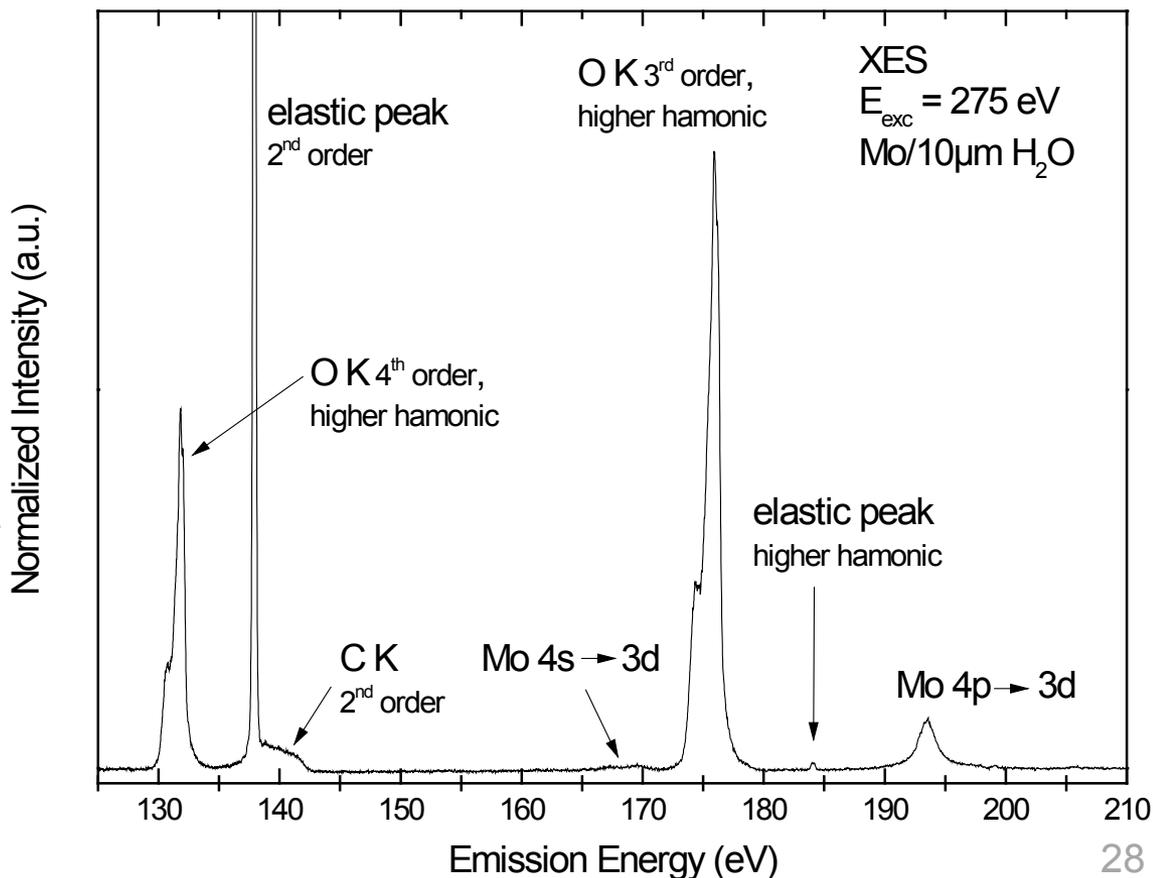
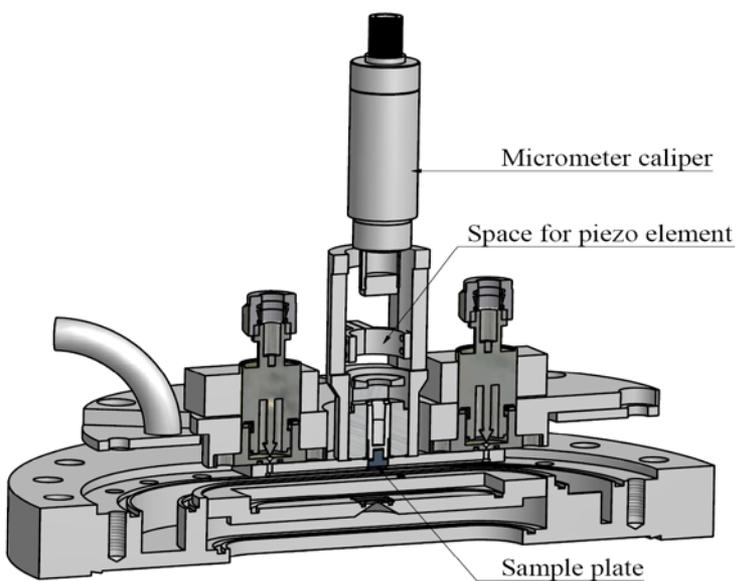
Very first results (**Accomplishments**)

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



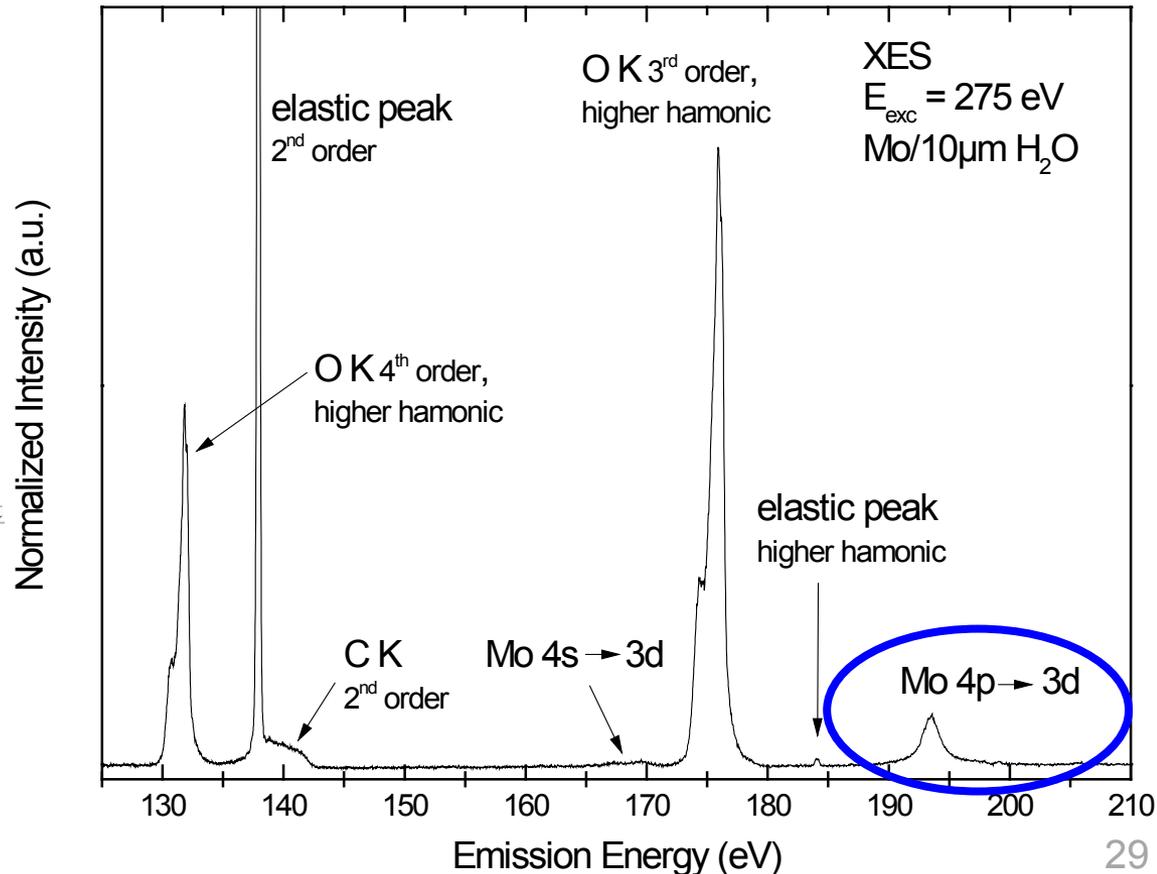
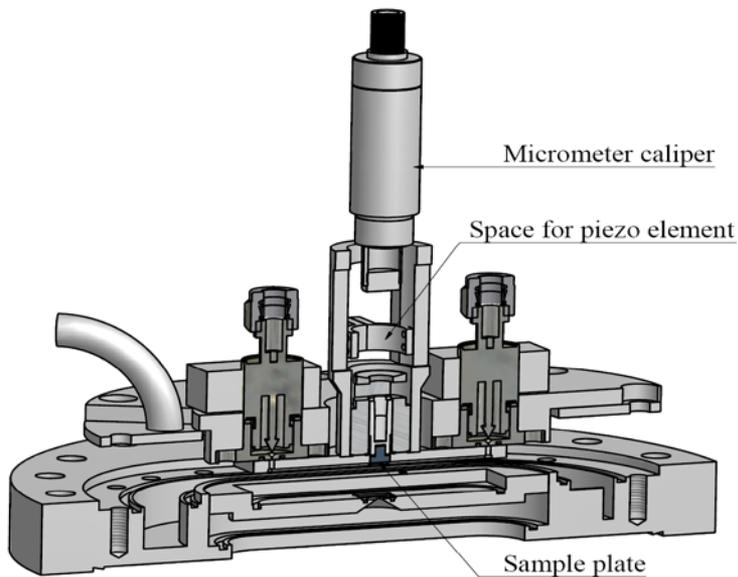
Very first results (**Accomplishments**)

- Developed prototype liquid-solid interface cell for XES in SALSA (to allow *in-situ* spectroscopy) – Mo metal reference under $10\ \mu\text{m}$ of H_2O



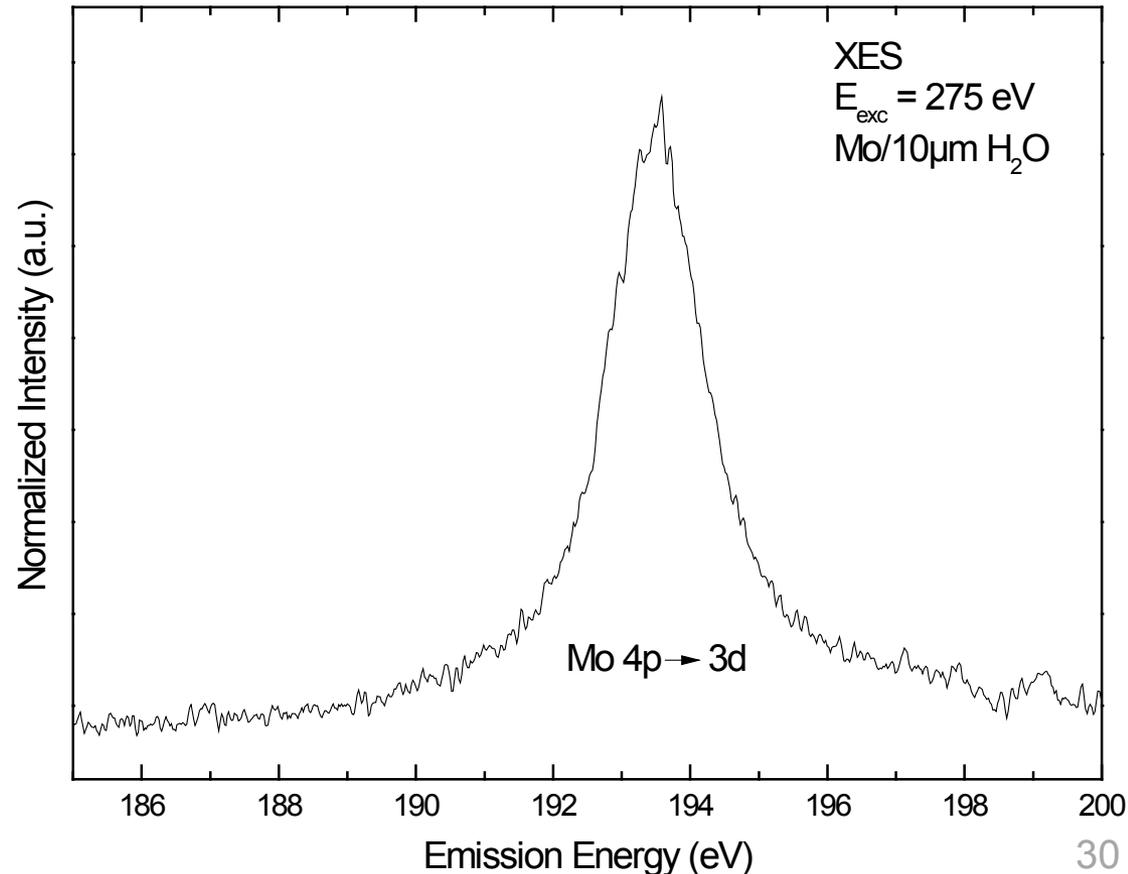
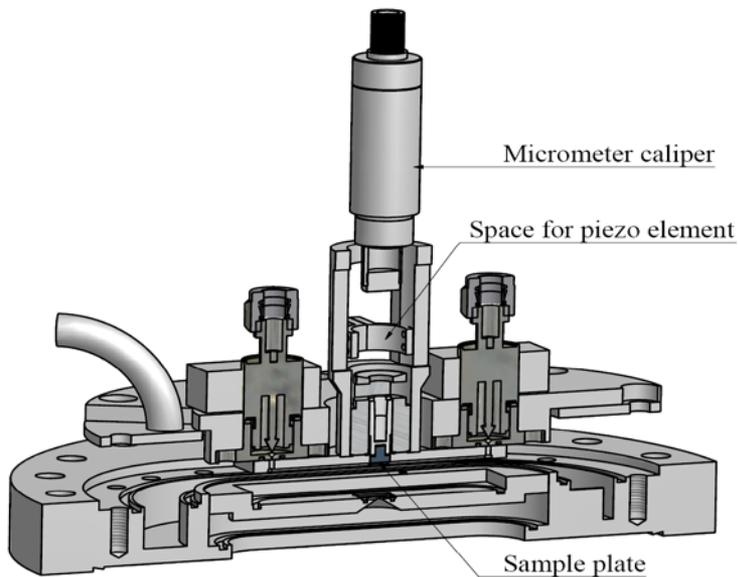
Very first results (Accomplishments)

- Developed prototype liquid-solid interface cell for XES in SALSA (to allow *in-situ* spectroscopy) – Mo metal reference under $10\ \mu\text{m}$ of H_2O



Very first results (**Accomplishments**)

- Developed prototype liquid-solid interface cell for XES in SALSA (to allow *in-situ* spectroscopy) – Mo metal reference under $10\ \mu\text{m}$ of H_2O



Electronic Structure of Fe₂O₃ Thin Films

With:

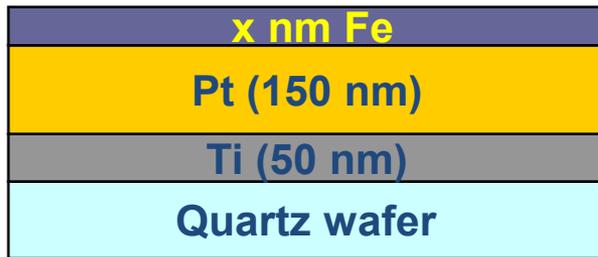
**A. Forman, A. Kleiman-Shwarsctein,
and Eric McFarland**

University of California, Santa Barbara

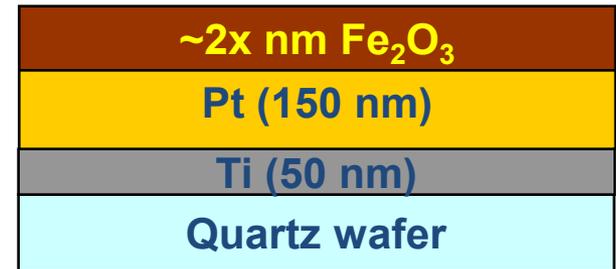


Sample Preparation (Approach)

“Real world” Film (UCSB)



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



Prototypical Films (UNLV)



Heated in partial O₂
• 600 C, 90 seconds

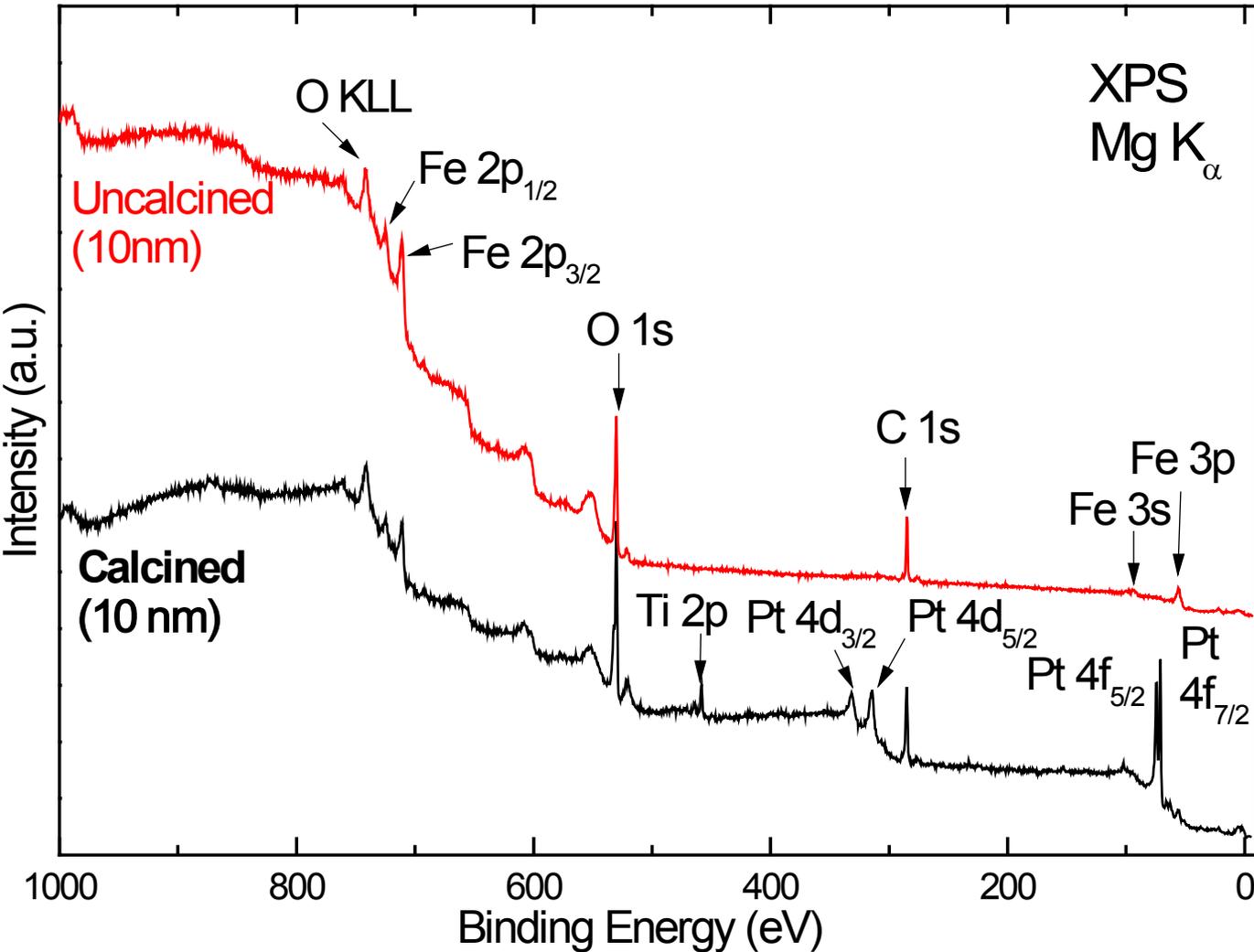


Heated in partial O₂
• 600 C, 3 minutes



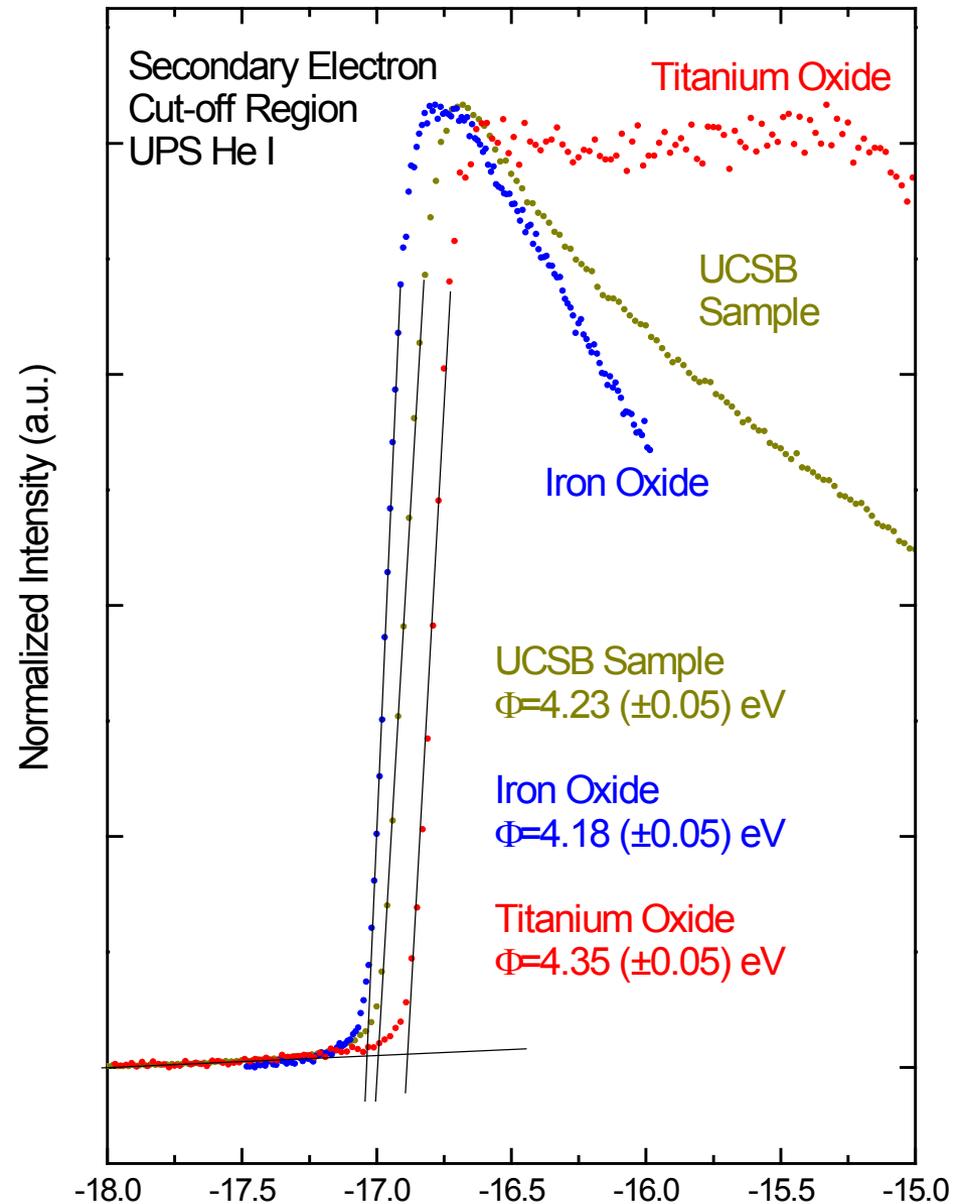
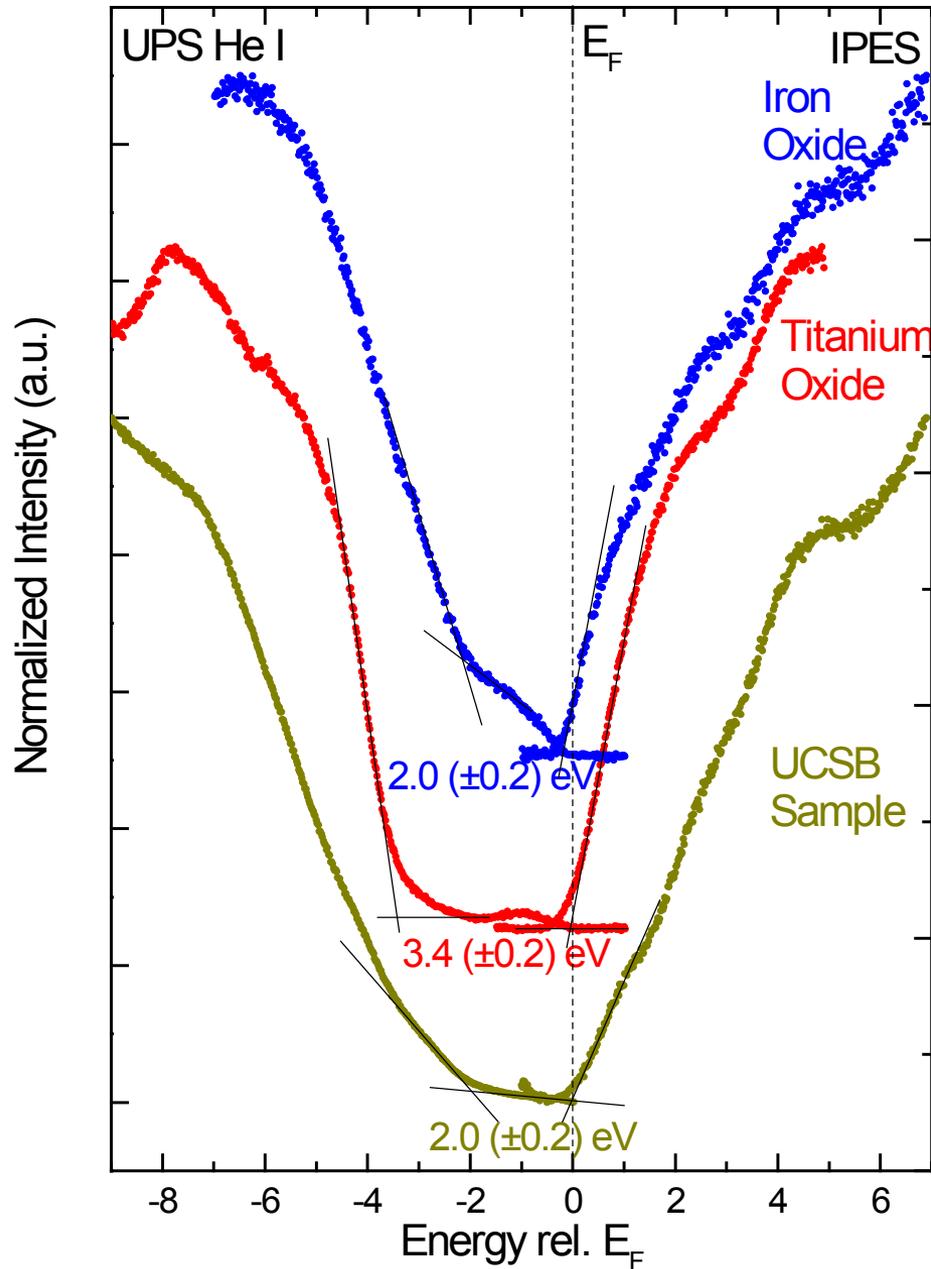
Effect of calcination on thin Fe_2O_3 samples

(FY 2010 Accomplishments)

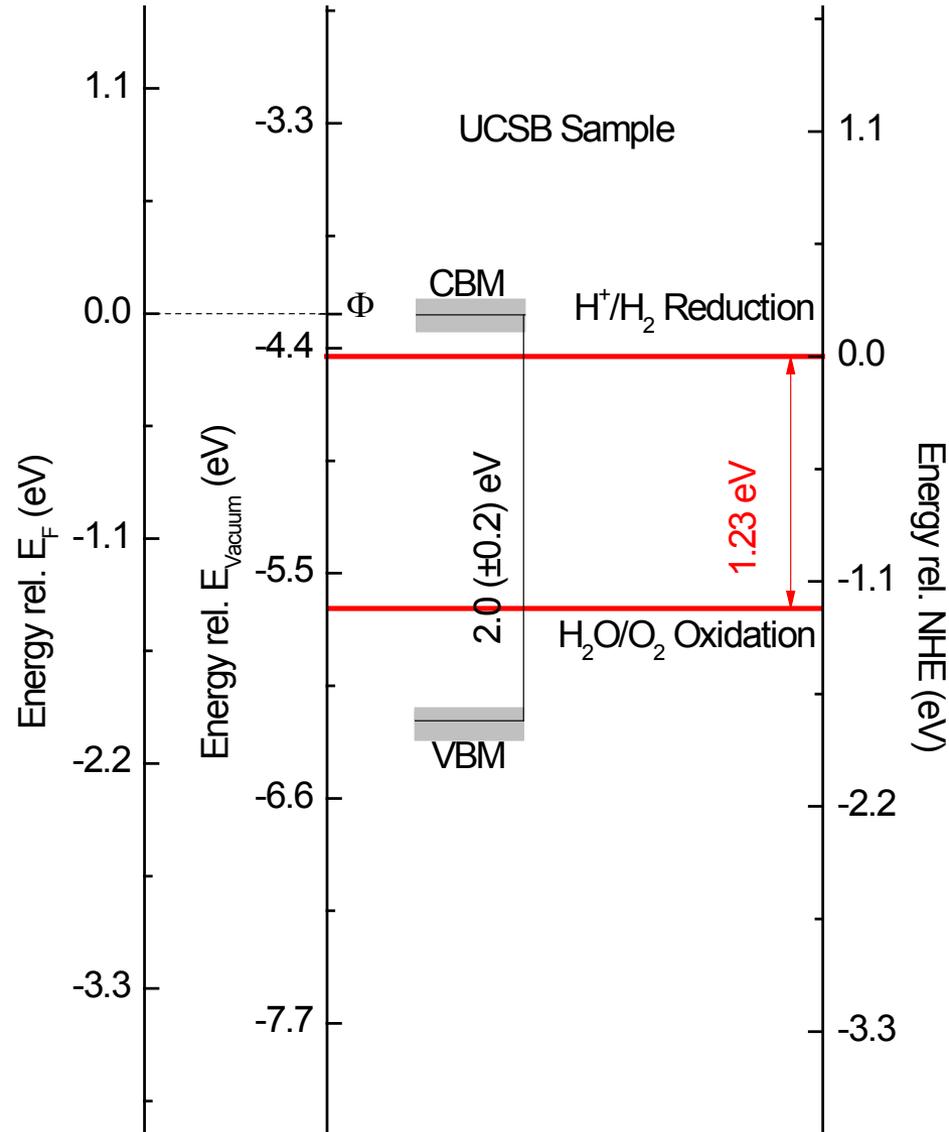
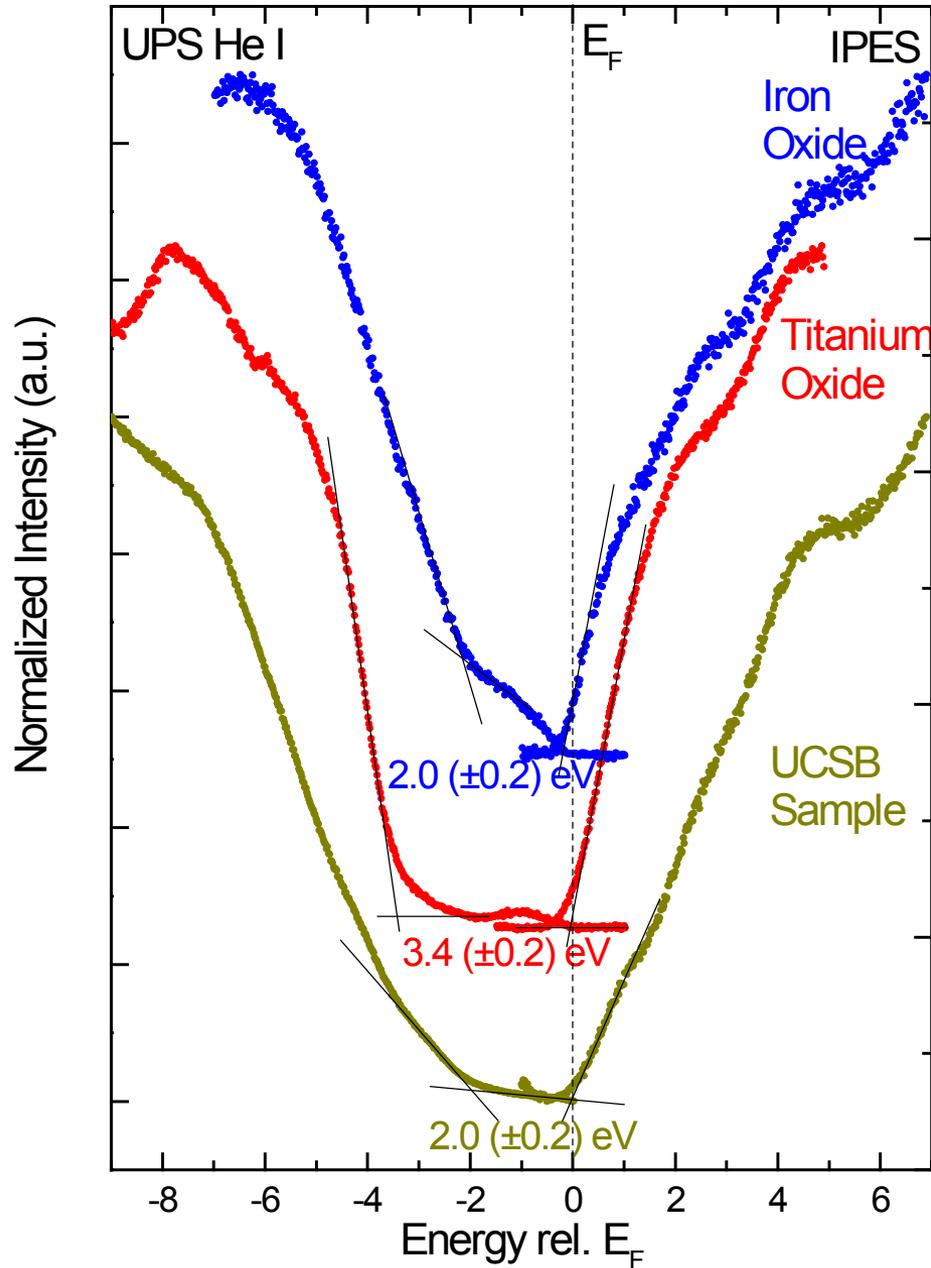


- Ti and Pt are detected at the surface after calcination
- Pt peaks not seen in thicker calcined samples (not shown)

Electronic surface structure (Accomplishments)



Electronic surface structure (Accomplishments)



Summary of Fe₂O₃ 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
 - WS₂ and MoS₂ with Stanford
 - WO₃ and Cu(In,Ga)Se₂ 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