Surface Validation: Physical and Electronic Characterization of Materials for Photoelectrochemical Hydrogen Production

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May 16, 2012

Project ID #
PD051

Overview

Timeline

- Project start date: 11/4/11
- Project end date: 11/2/12
- Percent complete: 42%

Budget

- Total project funding
  - DOE share: $150k
  - Contractor share: $0k
- Funding received in FY11: $0k
- Funding for FY12: $150k

Barriers

- Barriers addressed
  - Y. Materials Efficiency
  - Z. Materials Durability
  - AA. PEC Device and System Auxiliary Material

Partners

- Interactions/collaborations: DOE EERE PEC WG (in particular NREL and LLNL), Berkeley Lab, HZB Berlin, U Würzburg, KIT
- 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)**
  - **Discuss modifications (composition, process, …) with 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**

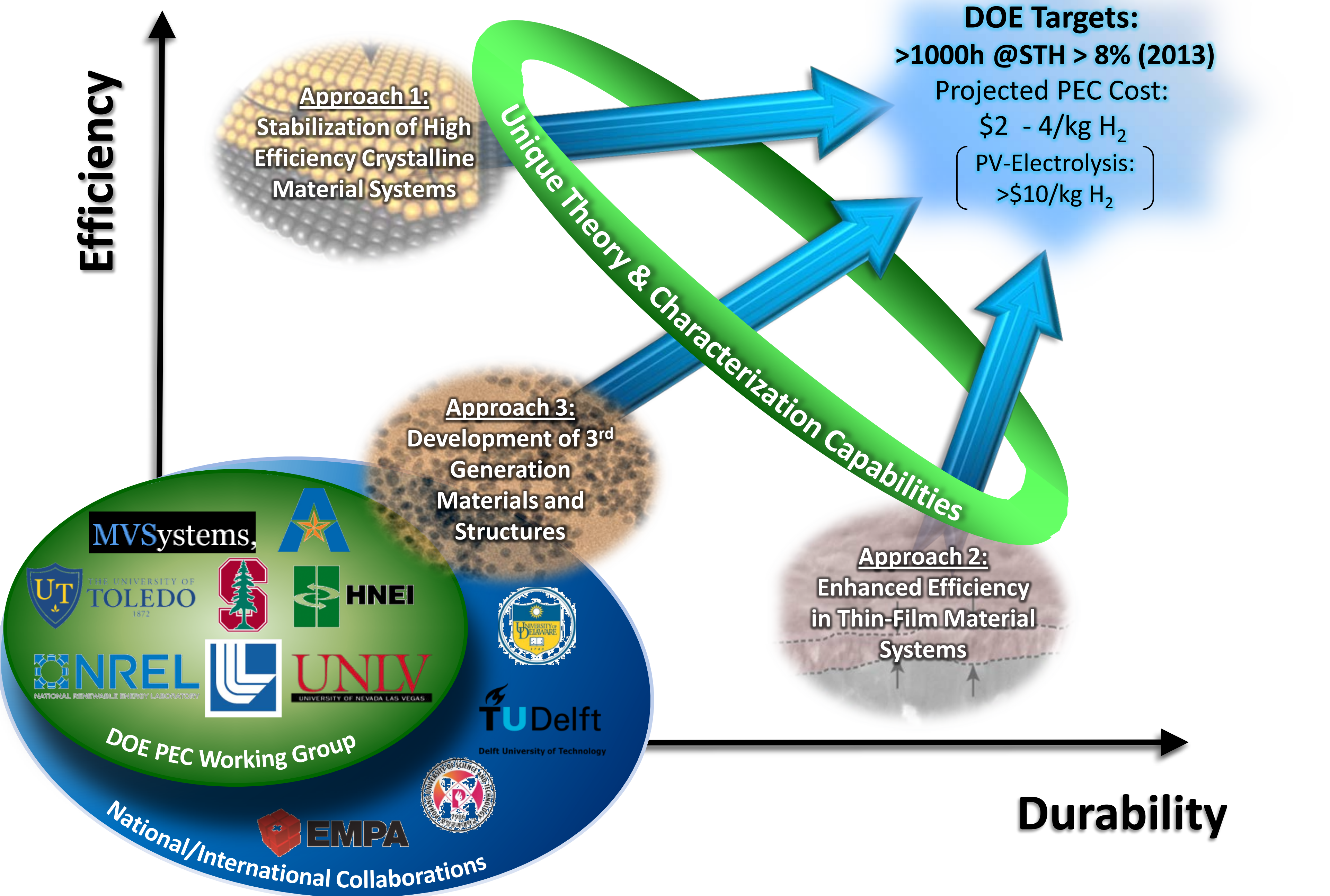
Collaborations

(Relevance, Approach, & Collaborations)

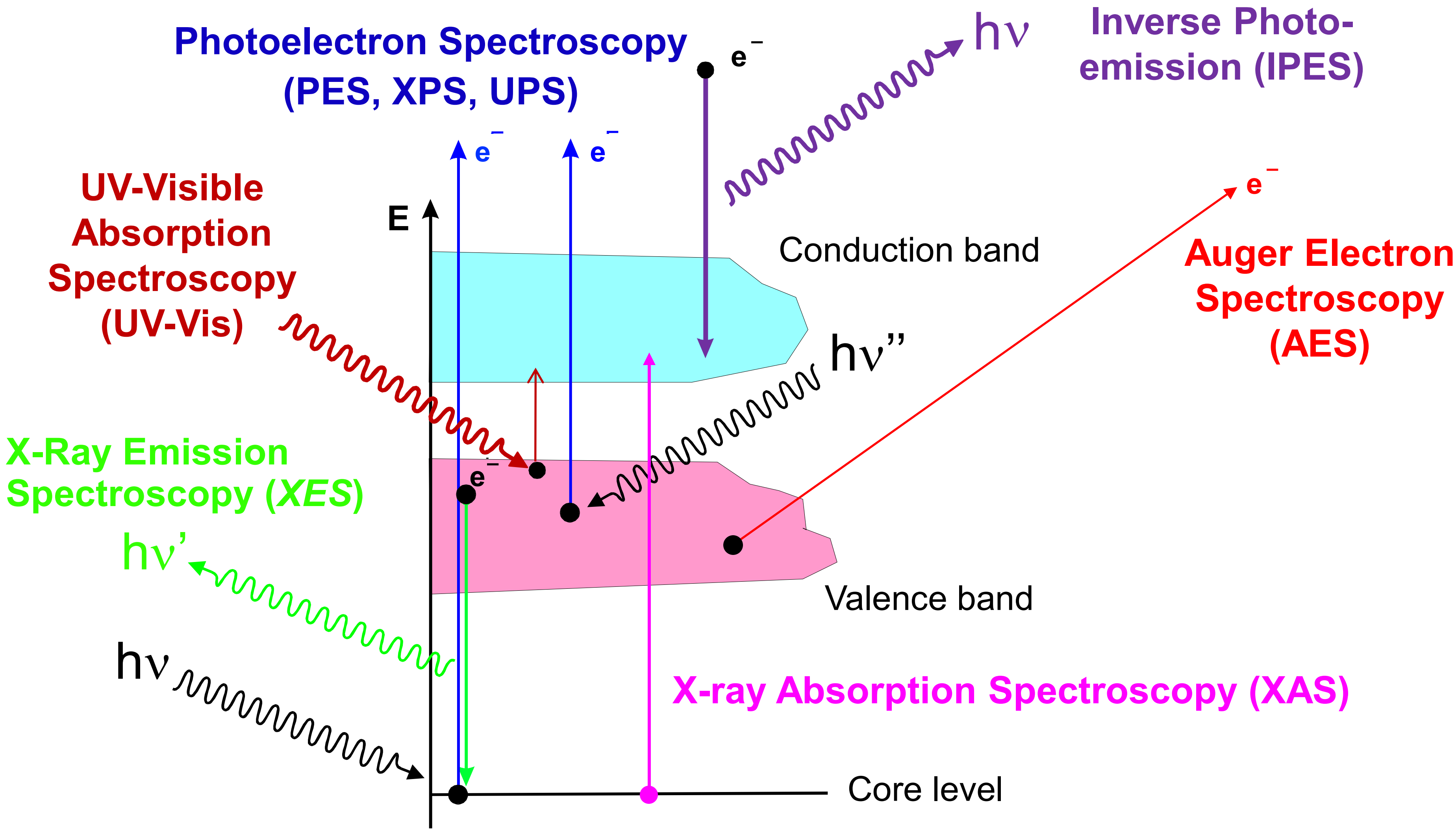
- **Collaborations are at the heart of our activities:**
  - Supply of samples
  - Most important: supply of open questions, issues, challenges
  - Interactive interpretation of results
  - Joint discussion of potential modifications
  - Involvement in implementing modifications
- **Great collaboration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

  Current project:
  - NREL: $(Ga,In)(P,N)_2$
  - LLNL: Theory ($(Ga,In)P_2$, liquid/solid interfaces)

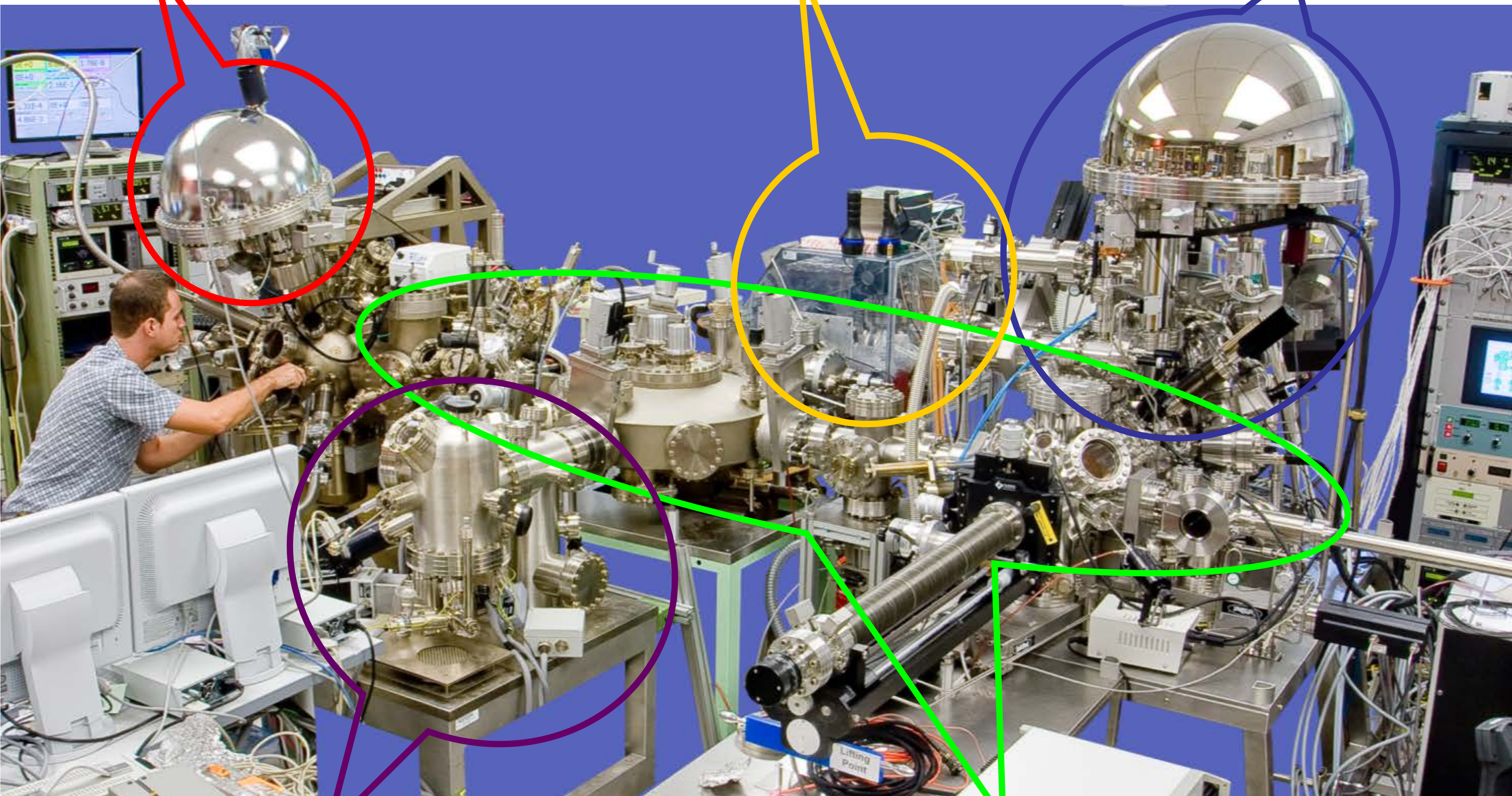
  Predecessor project:
  - Stanford U: MoS_2
  - U Hawaii/HNEI: WO_3, $W(X)O(Y)_3$, $Cu(In,Ga)(S,Se)_2$
  - UC Santa Barbara: Fe_2O_3 et al.
  - MVSystems: Si:C


DOE Targets:
>1000h @STH > 8% (2013)
Projected PEC Cost:
$2 - 4/kg H_2
PV-Electrolysis:
>$10/kg H_2
Efficiency
Durability
Approach 1:
Stabilization of High Efficiency Crystalline Material Systems
Unique Theory & Characterization Capabilities
Approach 3:
Development of 3rd Generation Materials and Structures
Approach 2:
Enhanced Efficiency in Thin-Film Material Systems
MVSystems,
THE UNIVERSITY OF TOLEDO 1872
HNEI
NREL
NATIONAL RENEWABLE ENERGY LABORATORY
UNLV
UNIVERSITY OF NEVADA LAS VEGAS
TU Delft
Delft University of Technology
EMPA
DOE PEC Working Group
National/International Collaborations

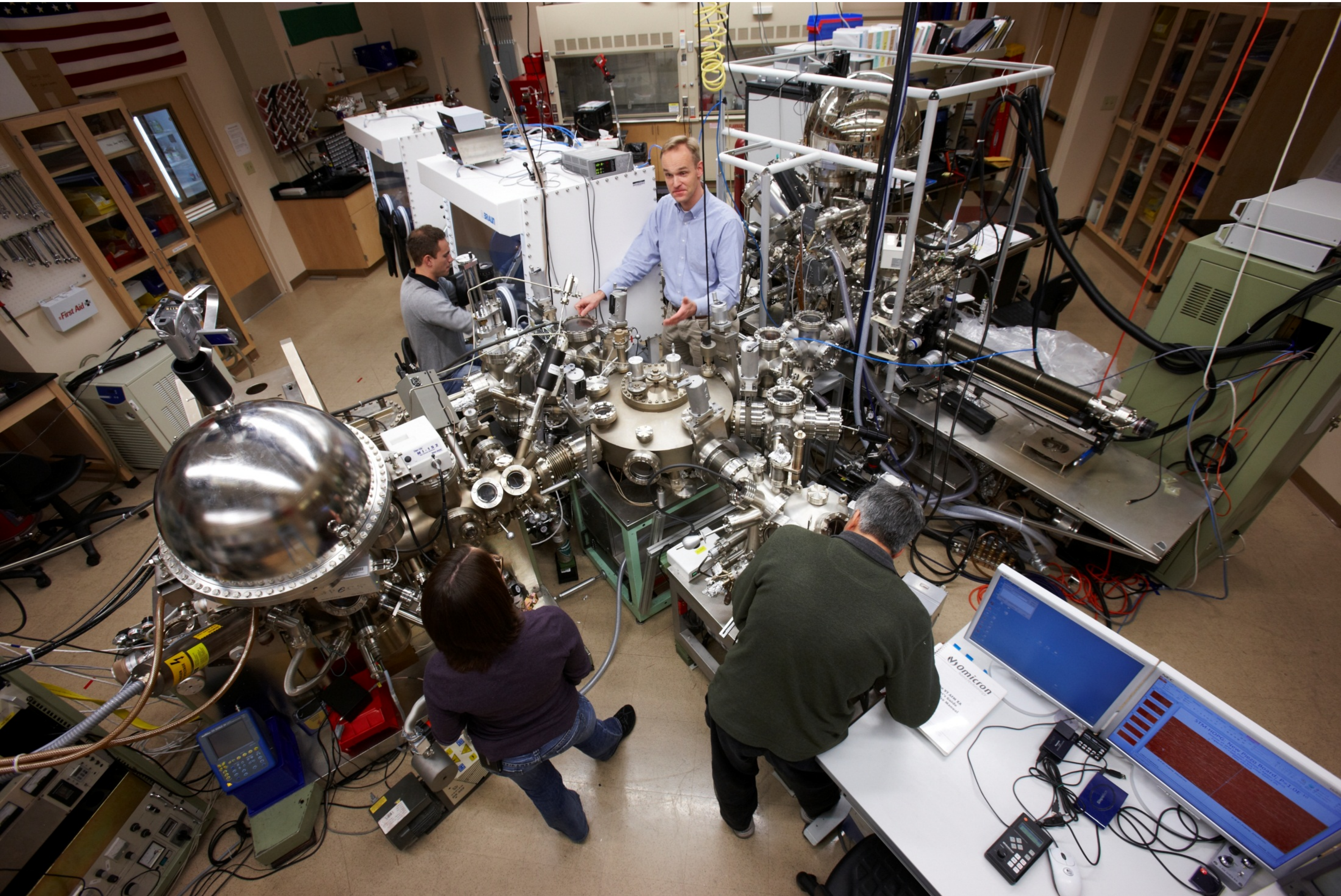
UV/Soft X-ray Spectroscopies *(Approach)*



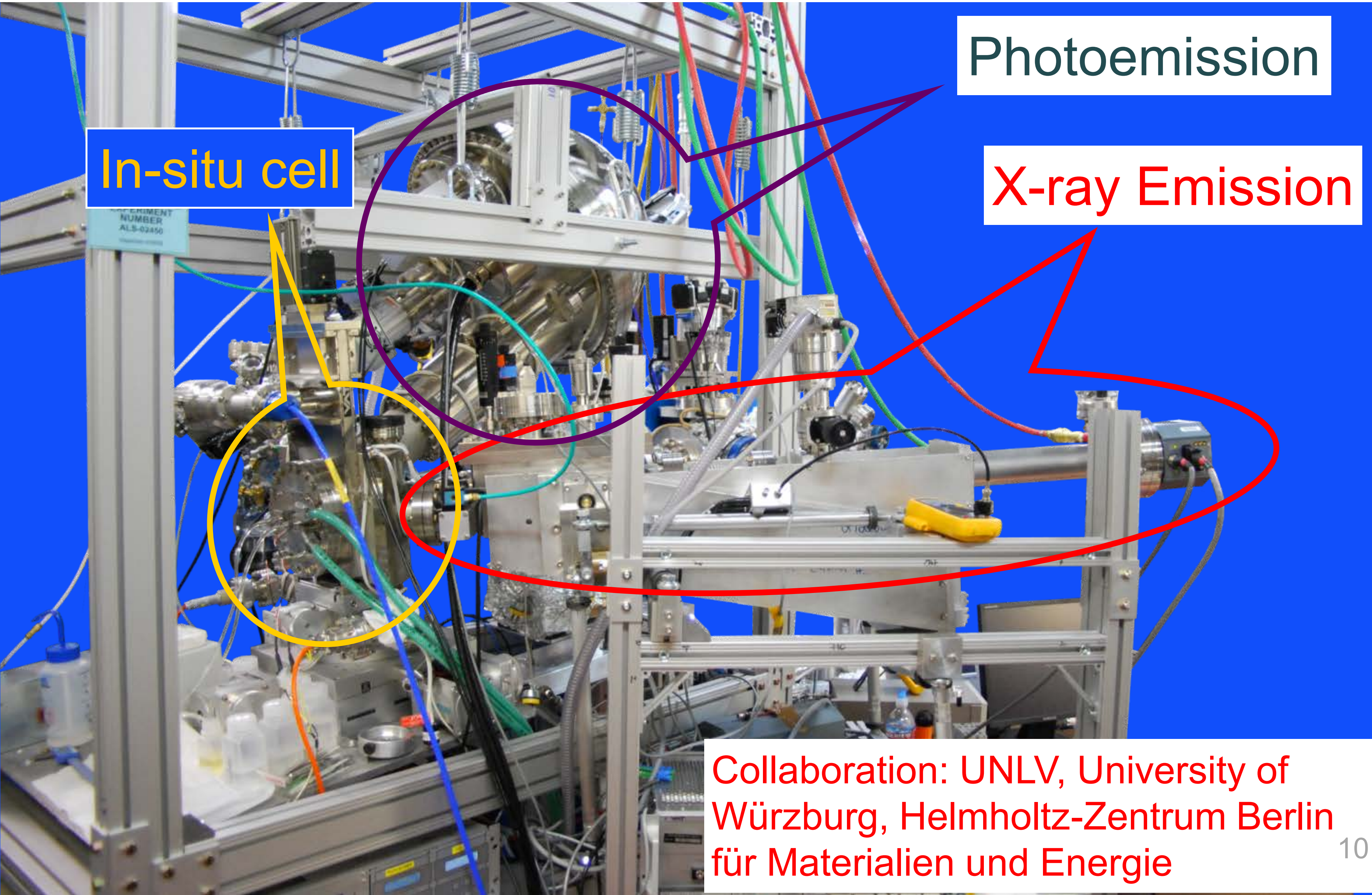
Plus: Atomic Force Microscopy


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

Relocation to a (much bigger and better) lab



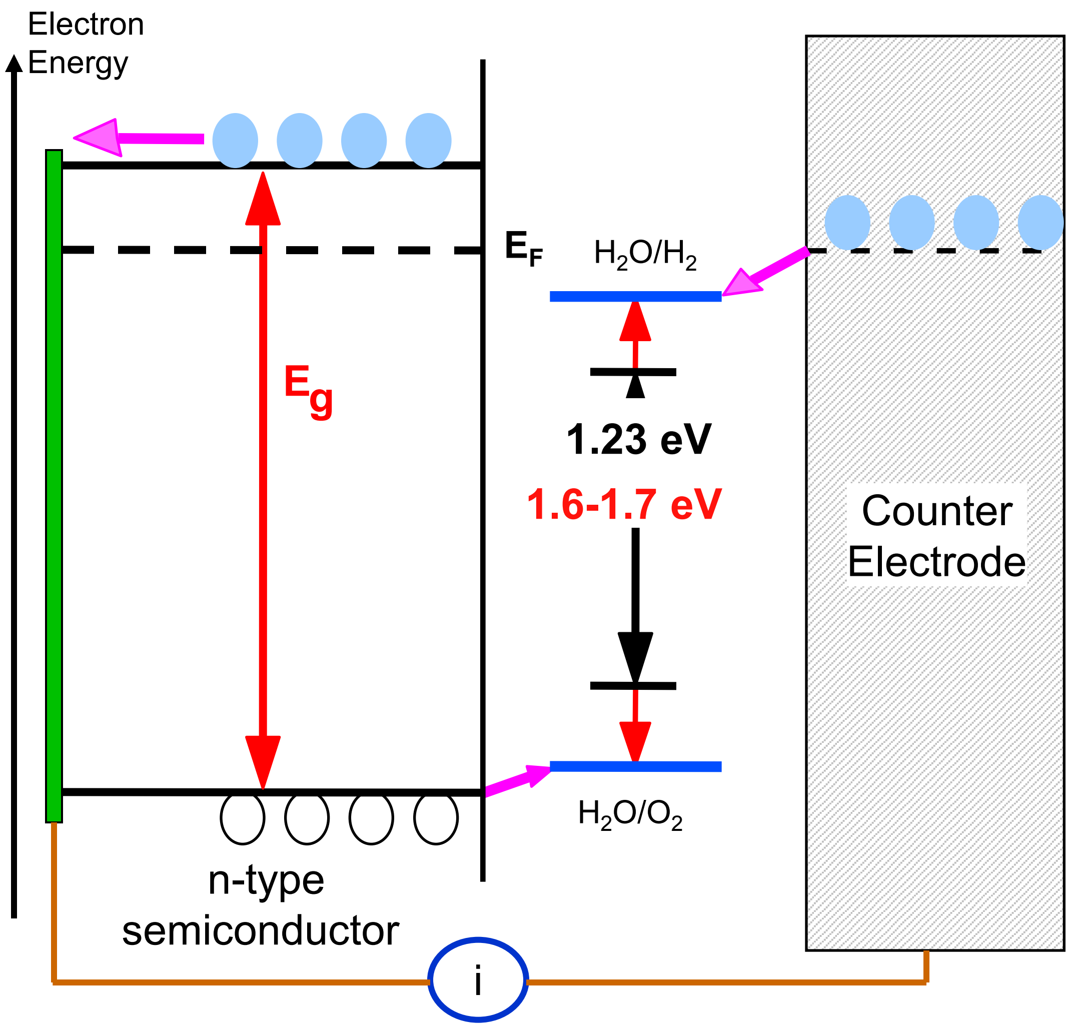
SALSA: Solid And Liquid Spectroscopic Analysis at Beamline 8.0, Advanced Light Source, LBNL



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!)

$(Ga,In)(P,N)_x$ thin films for PEC

With:

Todd Deutsch and John Turner

National Renewable Energy Laboratory

Tadashi Ogitsu, Brandon Wood, Woon Ih Choi

Lawrence Livermore National Laboratory

David Prendergast

Lawrence Berkeley National Laboratory

For more details, please see PD035 and PD058

Main Tasks

(Relevance)

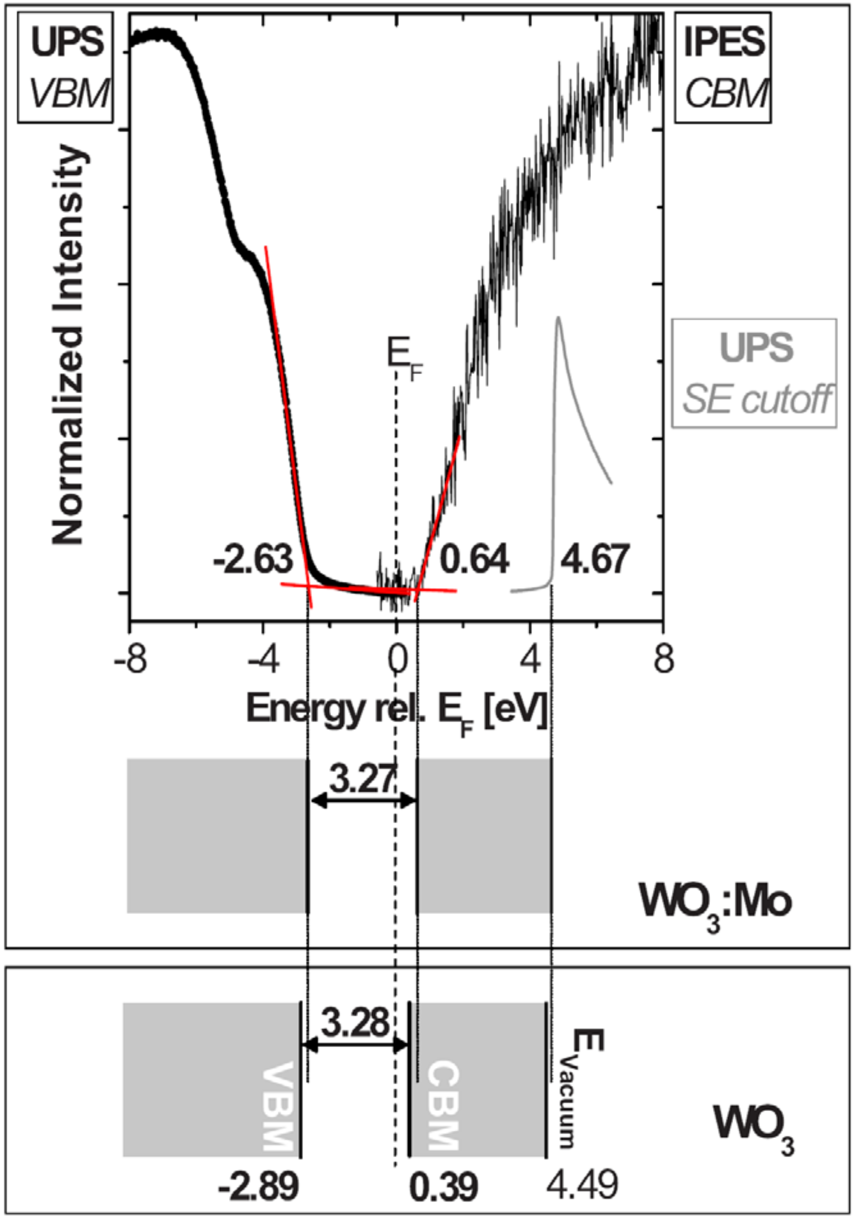
1. **Determine the benchmark electronic structure of $(Ga,In)P_2$ surfaces**

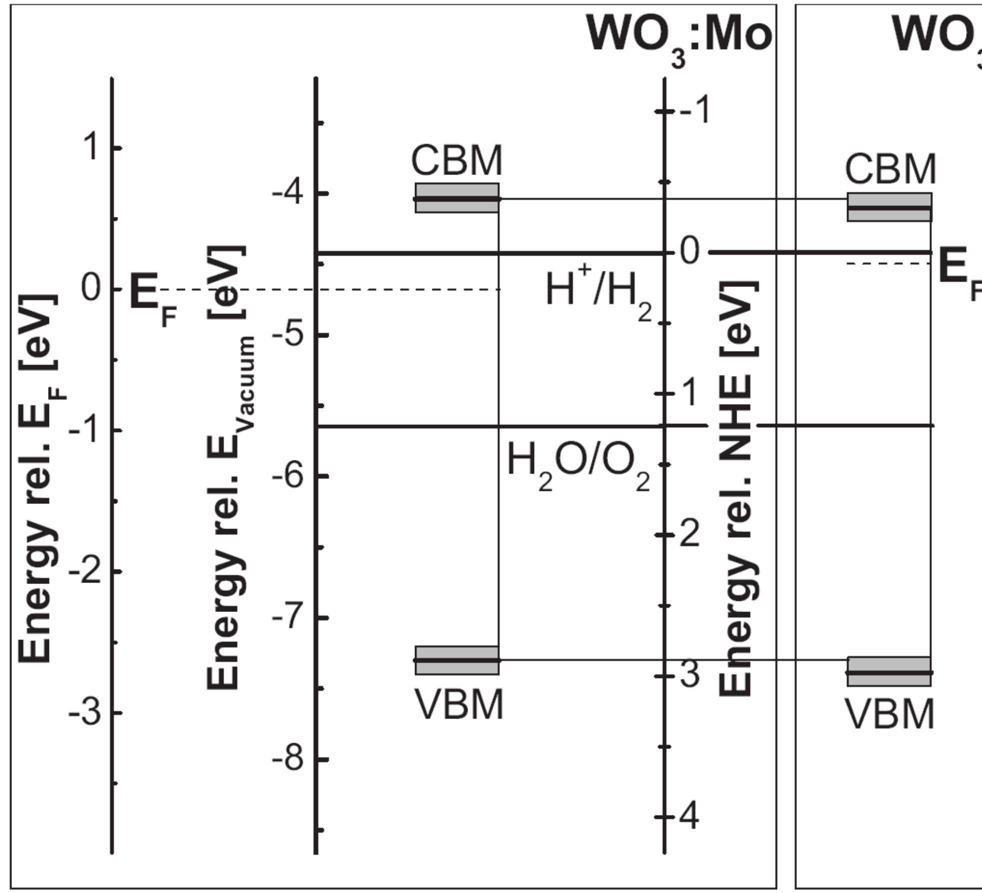
2. Investigate impact of N-treatment on $(Ga,In)P_2$ surfaces

3. Correlate spectroscopy with theory to establish base for predictive capabilities

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

(FY 2010 Accomplishments)



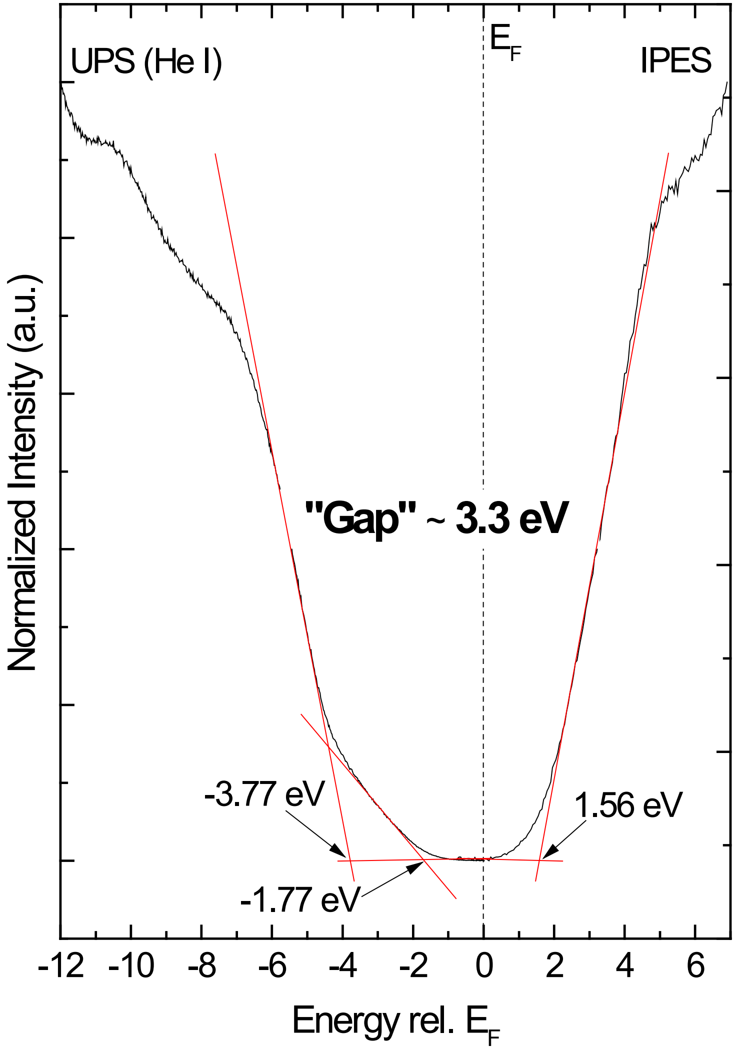


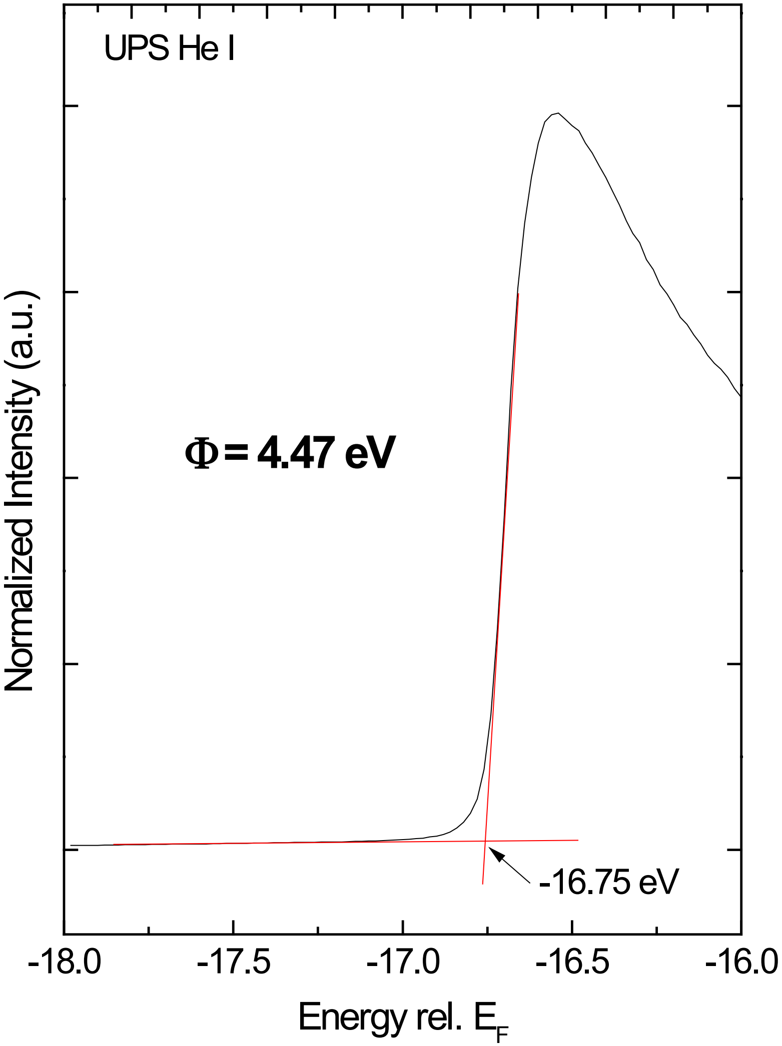
HNEI

APL **96**, 032107 (2010)

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

(FY 2011 Accompl.)





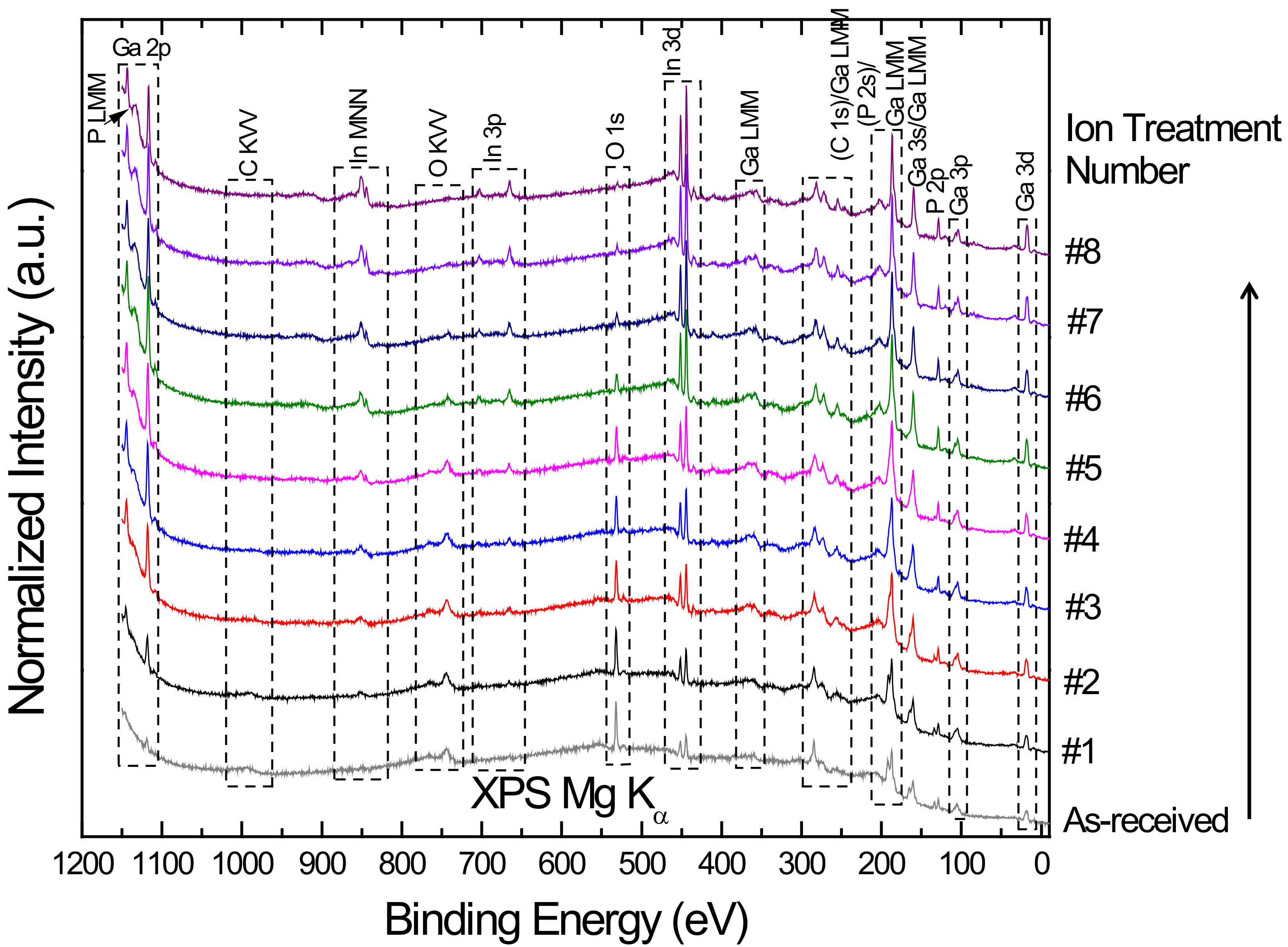
- Surface-sensitive measurements are powerful, but are also influenced by surface adsorbates
- HOMO-LUMO energy separation of surface adsorbates ("band gap"): ~ 3.3 eV
- Compare: UV-Vis and photocurrent spectroscopy (NREL): ~ 1.8 eV
- Work function of surface adsorbates: ~ 4.5 eV
- Current work: optimize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

Need for Surface Cleaning: Low-Energy Ion Treatments of an air-exposed (Ga,In)P_2 film (50 eV Ar^+ ions)

Treatment Number	Length of Time Under 50 eV Ar^+ Ion Treatment	Cumulative Time Under 50 eV Ar^+ Ion Treatment
As Received	0	0
#1	15 minutes	15 minutes
#2	30 minutes	45 minutes
#3	30 minutes	75 minutes
#4	1 hour	135 minutes
#5	2 hours	255 minutes
#6	2 hours	375 minutes
#7	2 hours	495 minutes
#8	4 hours, 30 minutes	765 minutes

(Approach)

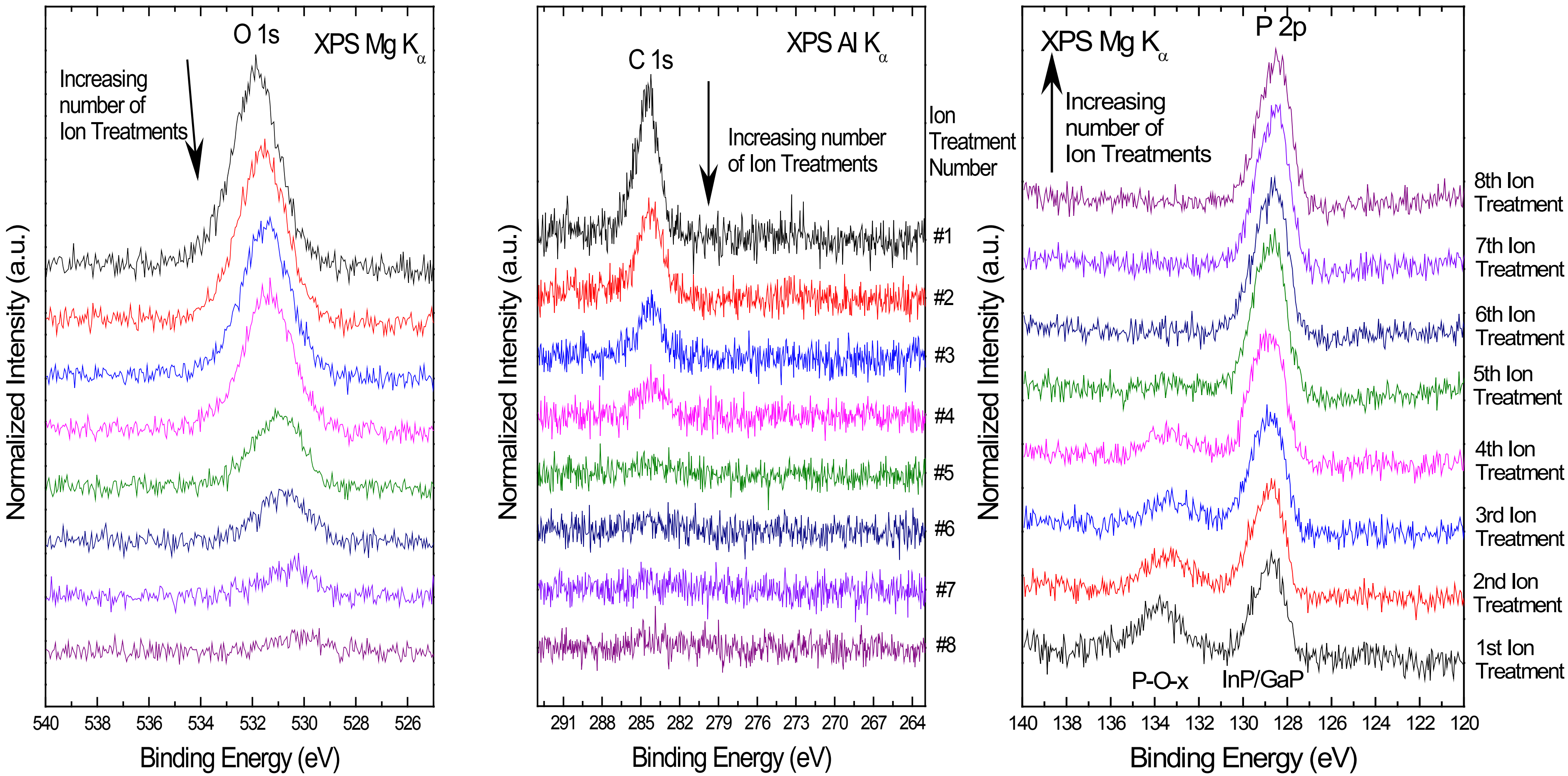
XPS Survey Spectra *(Accomplishments)*



Increase of Ga, In, P signals; decrease of C, O as a function of treatment time

Low-Energy Ion Treatments of an air-exposed $(Ga,In)P_2$ film: XPS detail spectra of C, O, and P

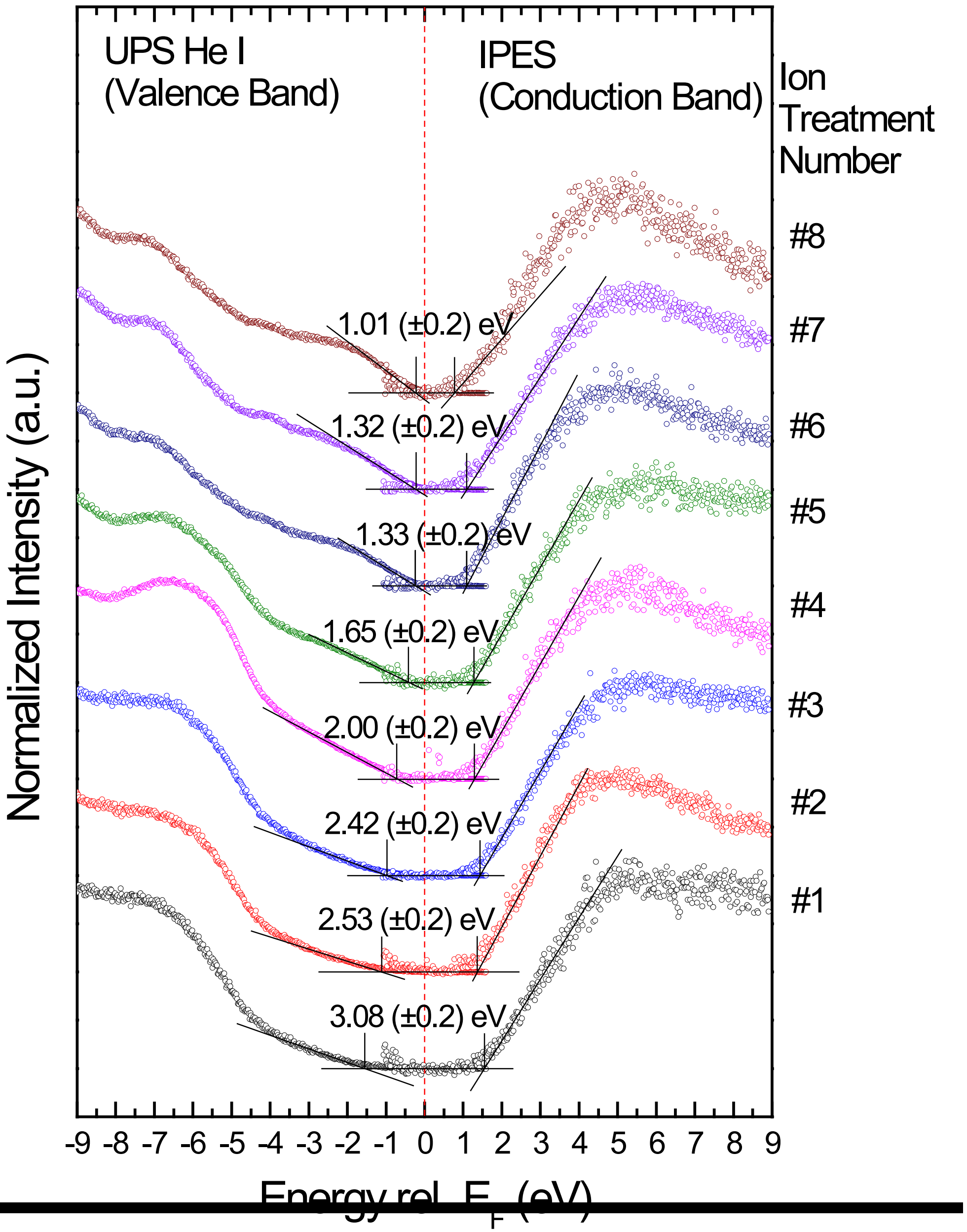
(Accomplishments)

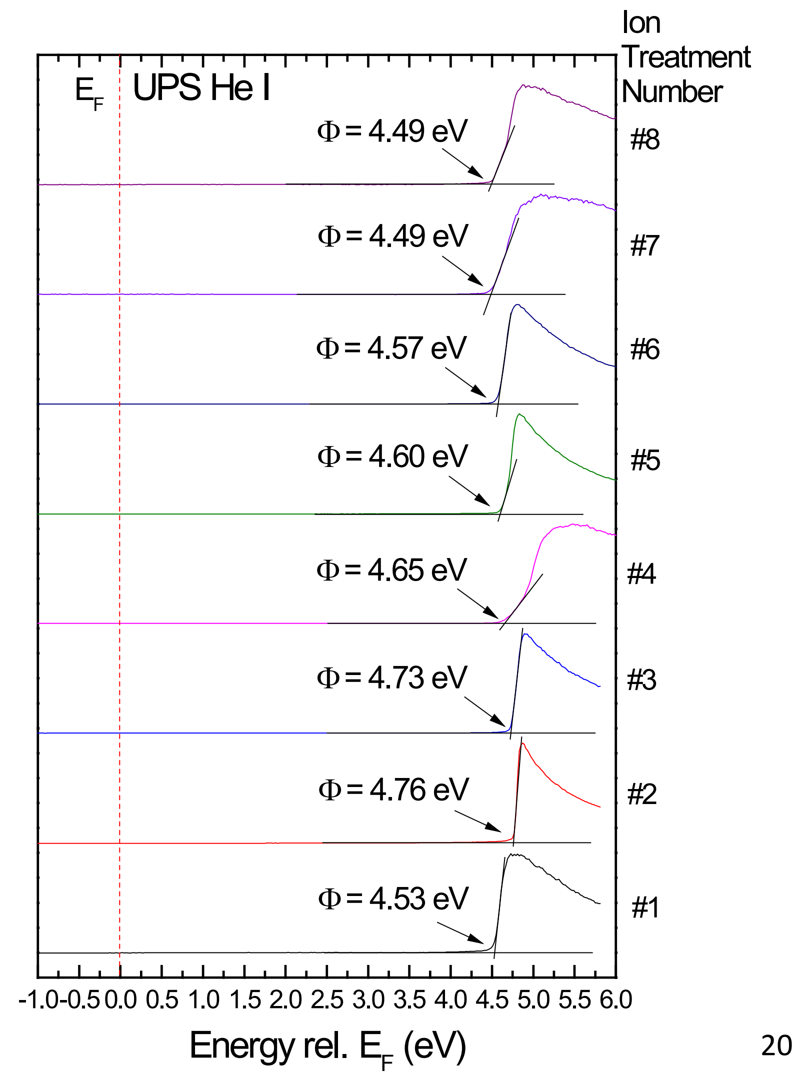


Essentially complete removal of O, C, and P-O-x signals (good!).
But is the surface damaged?

Band edges, gap, and work function (Accomplishments)

- Band gap narrows with treatment
- Fermi energy shifts towards the VBM
- Work fct. first increases, then decreases
- When is the surface clean? (Bulk: 1.75 eV)





Need for Pristine Starting Materials without Air-Exposure

Surface Validation: Progress in establishing baseline spectra of uncorroded surfaces for comparison

- **At NREL**
  - Nitrogen purged glove bag attached to synthesis reactor
  - Metal Organic Chemical Vapor Deposition (MOCVD) synthesis of 2µm thick p-$GaInP_2$ epilayer
  - Packaged under nitrogen with off-the-shelf vacuum seal device and shipped to UNLV
  - John Geisz, Waldo Olavaria from NREL PV center

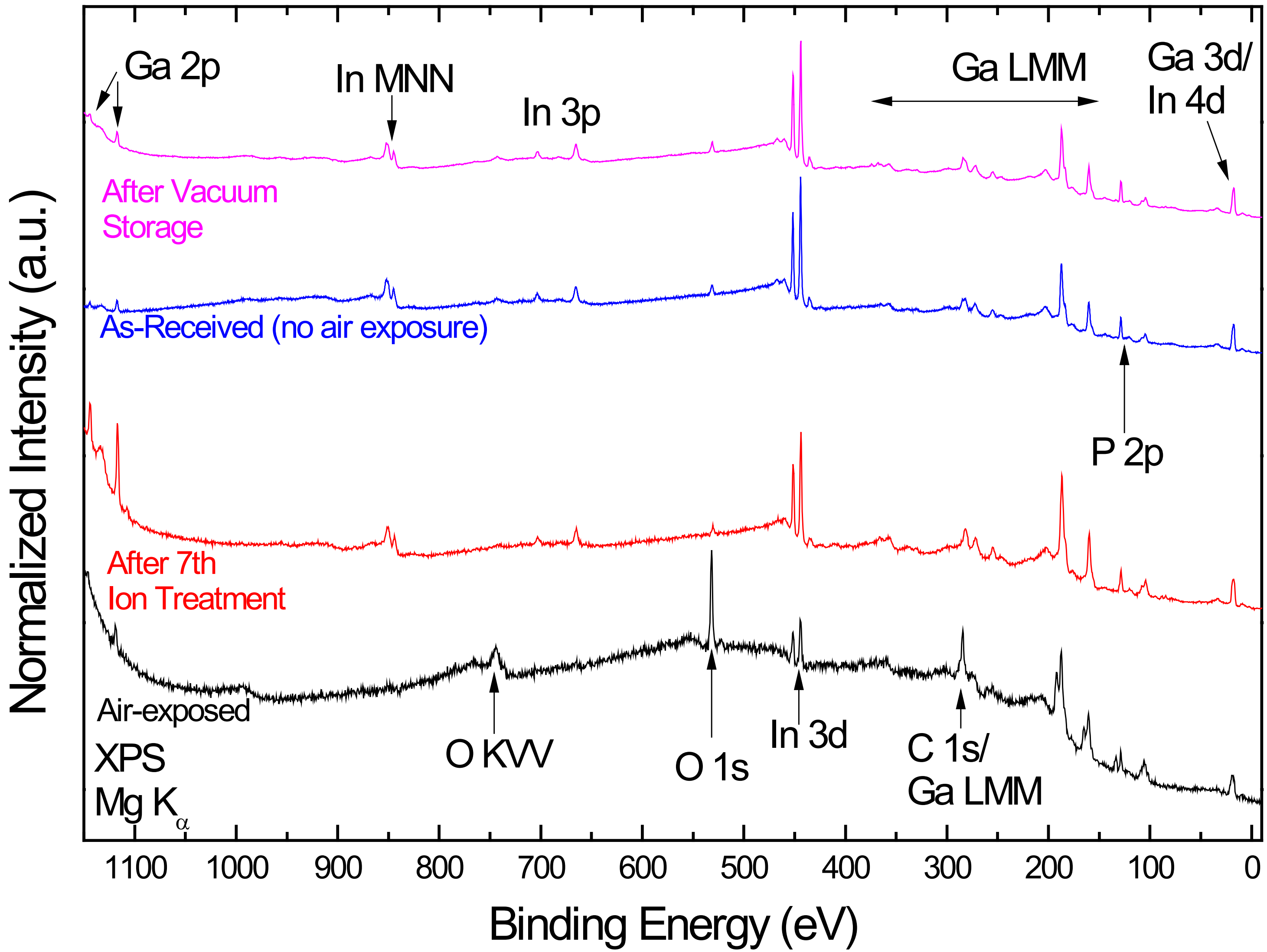
- **At UNLV**
  - Opened in glove box and introduced into UHV for analysis
  - XPS, UPS, IPES at UNLV

(Accompl.)

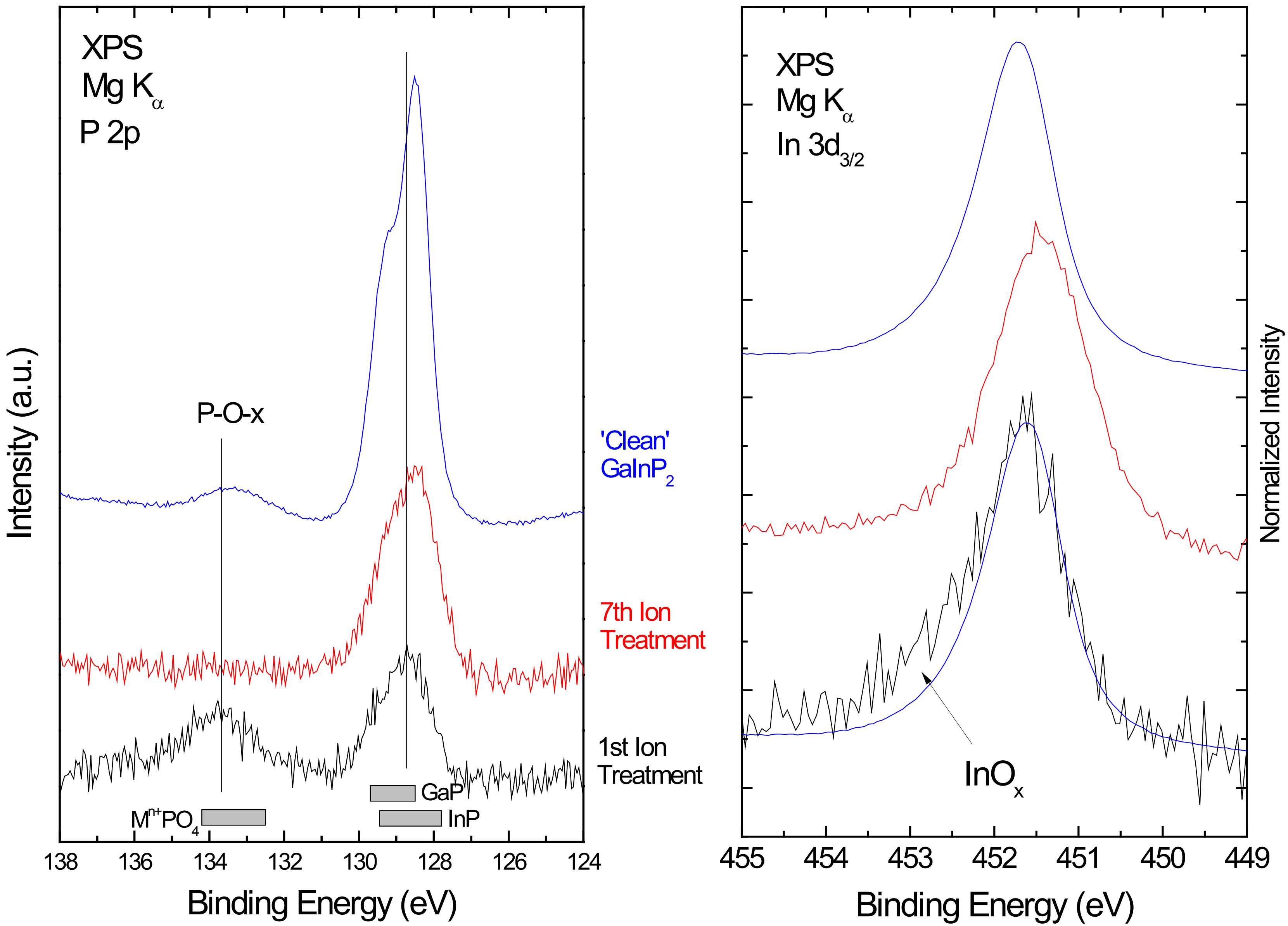
See talk PD035!

XPS survey spectra of two (Ga,In)P_2 samples using different sample handling

(Accomplishments)

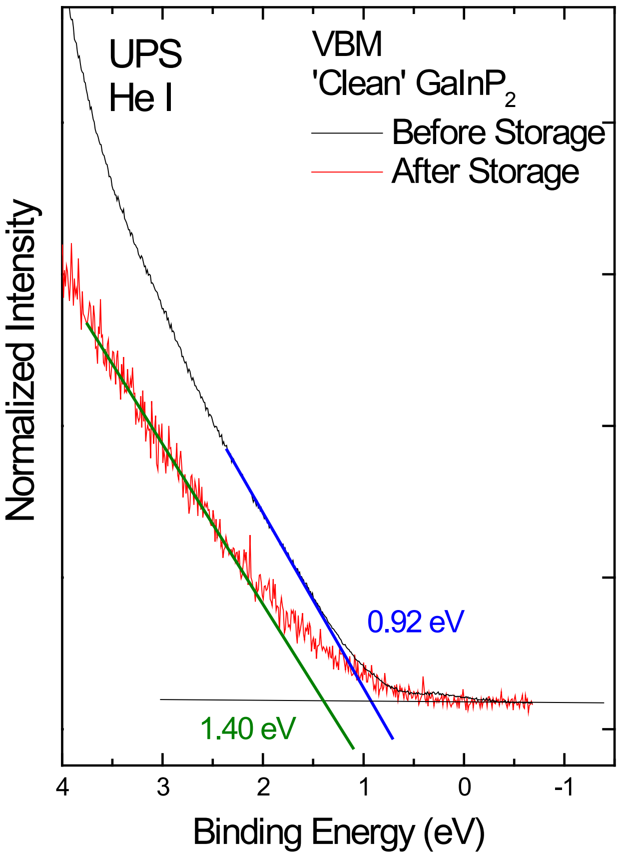


Air-exposed, ion-treated, and "clean" (Ga,In)P_2 surfaces: XPS detail spectra of P and In (Accompl.)

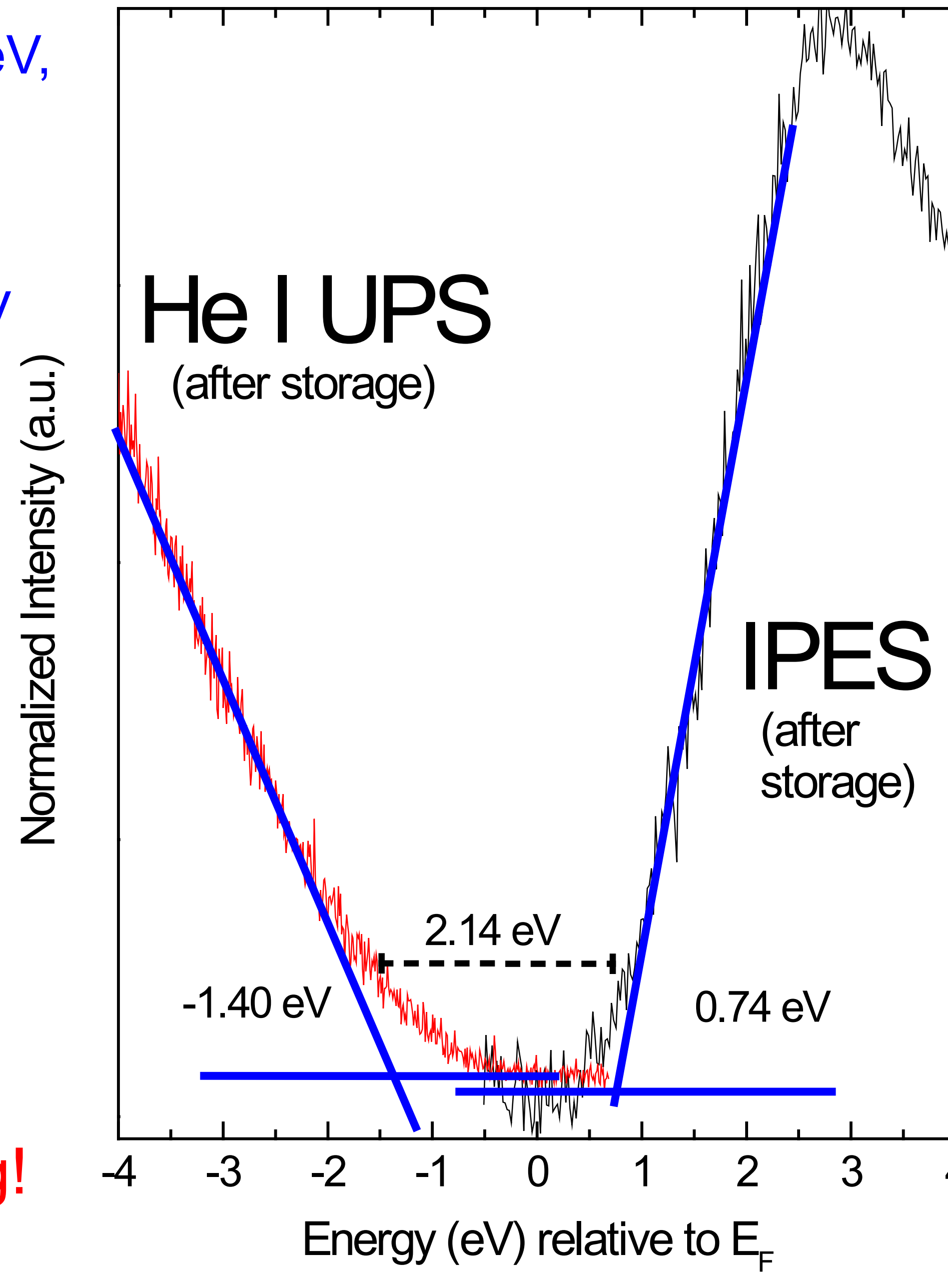


Band gap of "clean" (Ga,In)P_2 (Accomplishments)

- VBM after sample transfer: 0.92 eV, shifts to 1.40 eV after storage in UHV (due to IPES problems)
- CBM after storage: 0.74 eV
- Gap: 2.14 (or 1.66 eV?) ± 0.20 eV
- Bulk gap (lit.): 1.75 eV



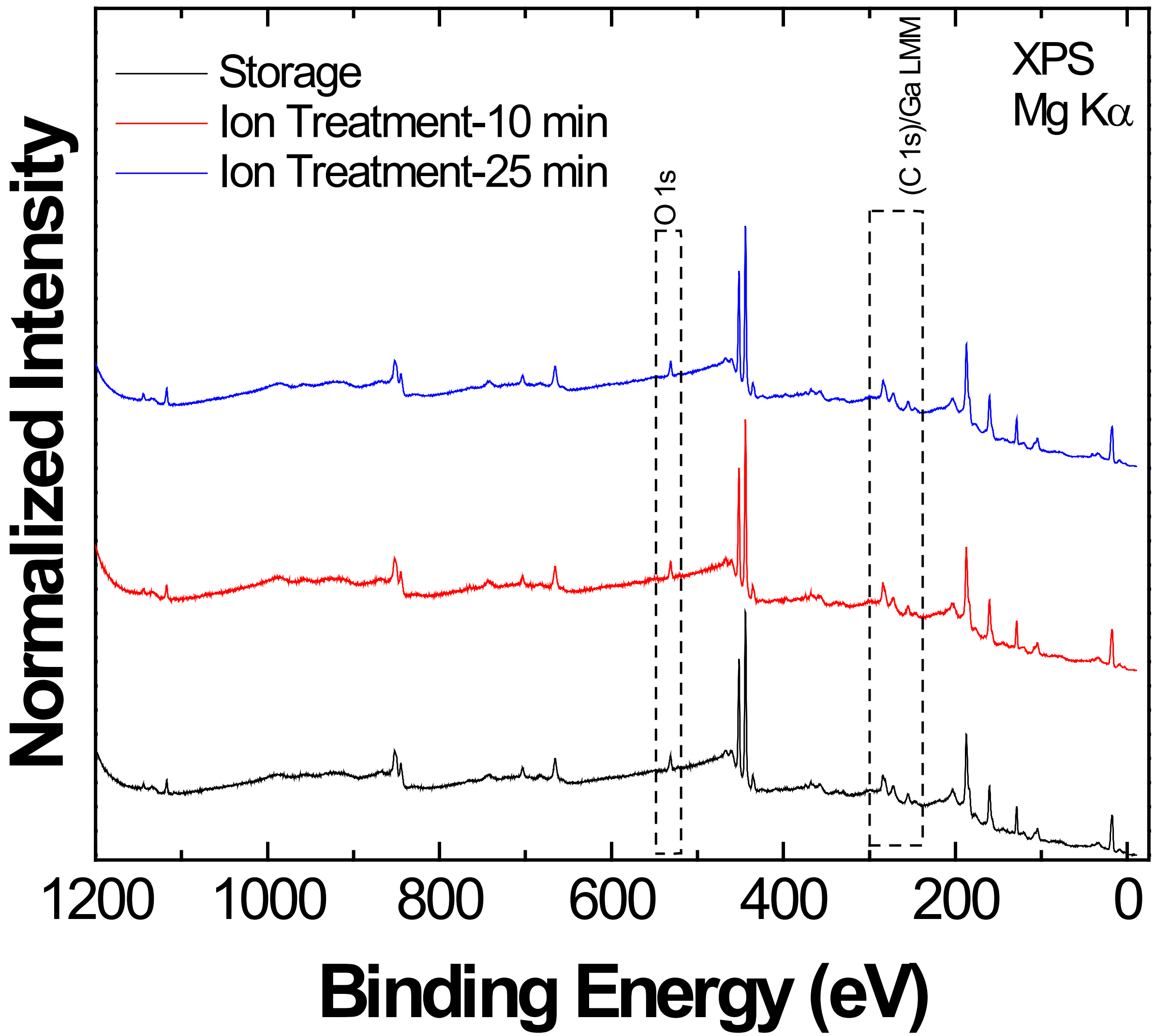
Need (some) surface cleaning!

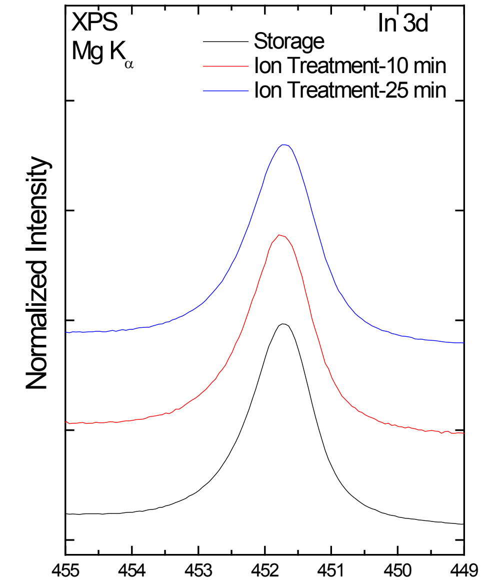


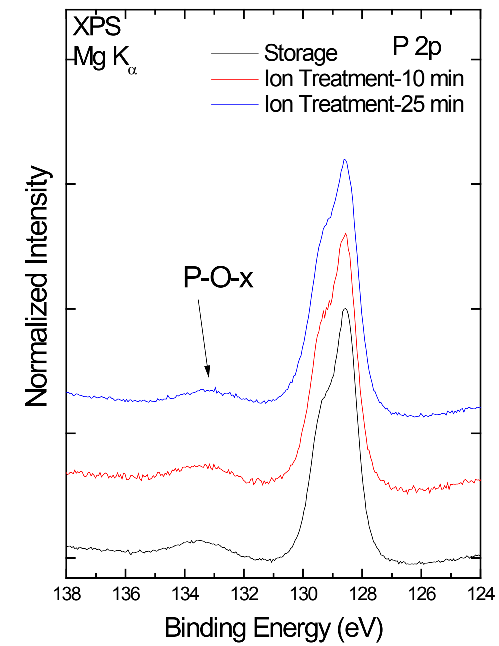
Need for (some) Surface Cleaning: Low-Energy Ion Treatments of "clean" (Ga,In)P_2 film (50 eV Ar^+ ions)

work currently ongoing

(Accompl.)







Main Tasks

(Relevance)

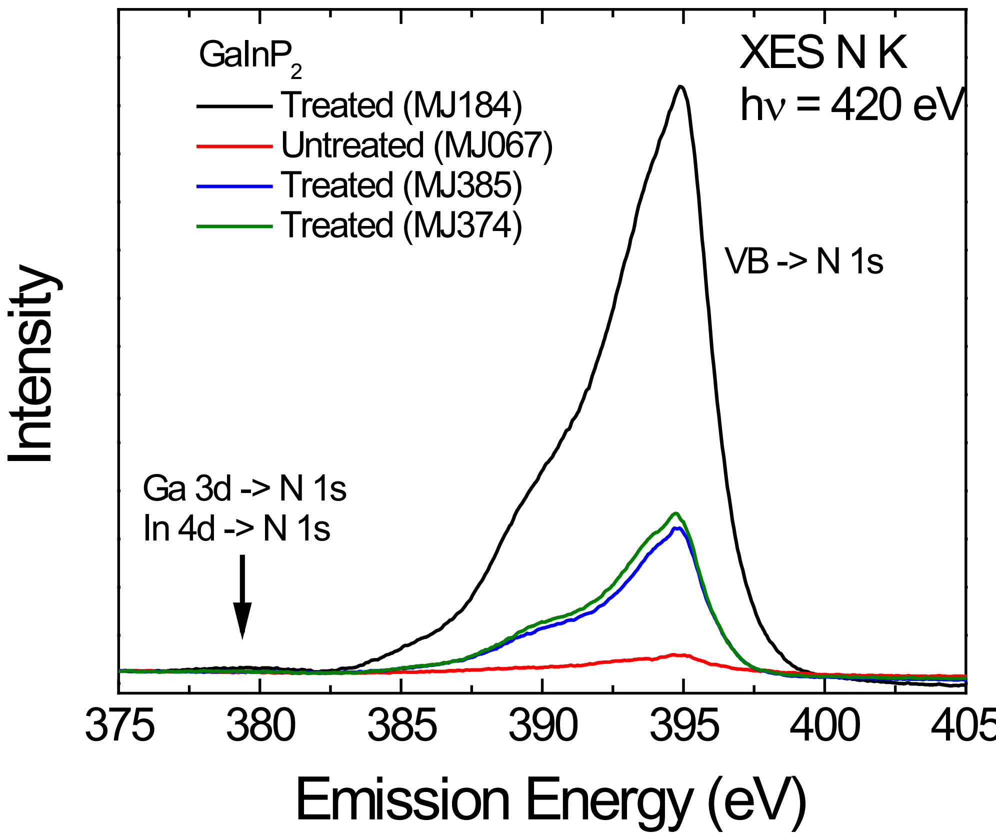
1. Determine the benchmark electronic structure of (Ga,In)P_2 surfaces

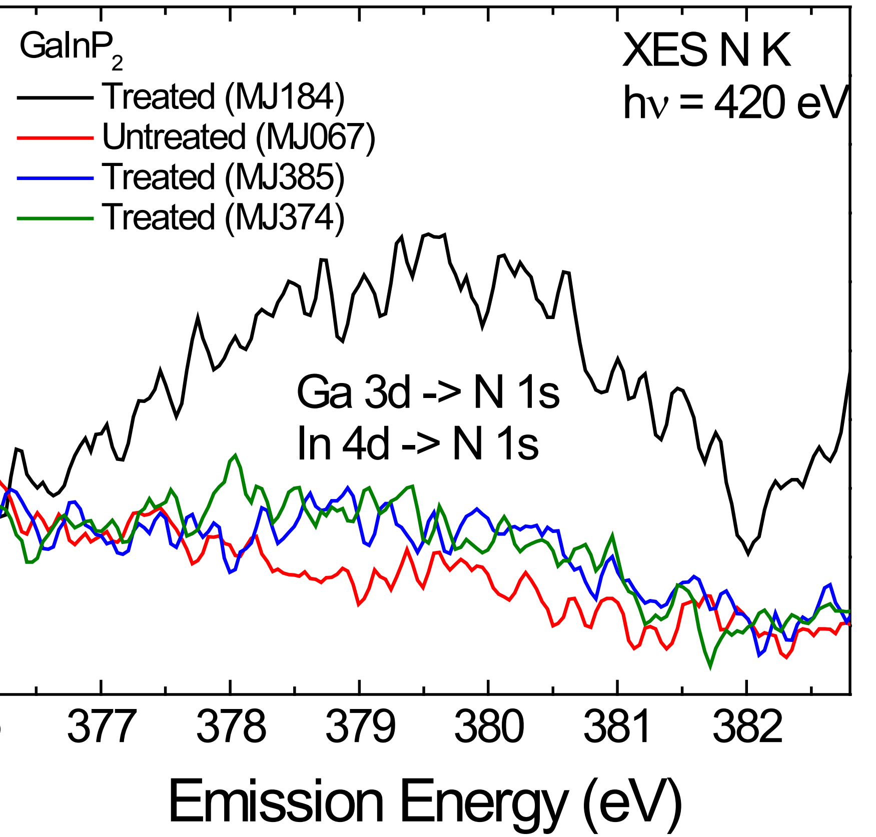
2. **Investigate impact of N-treatment on (Ga,In)P_2 surfaces**

3. Correlate spectroscopy with theory to establish base for predictive capabilities

Impact of N-treatment on (Ga,In)P_2 surfaces

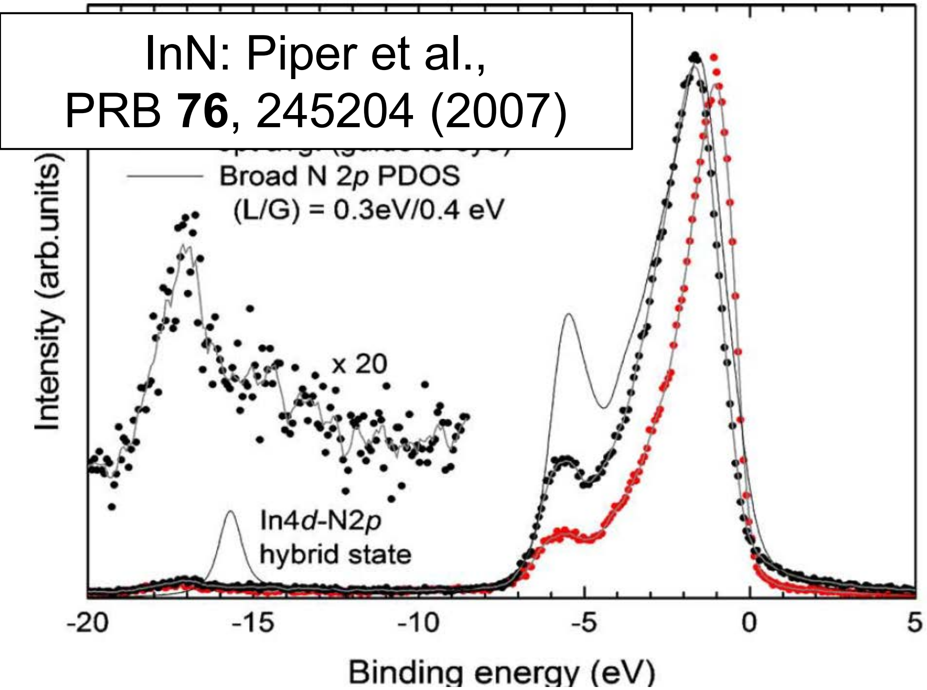
(Accomplishments)

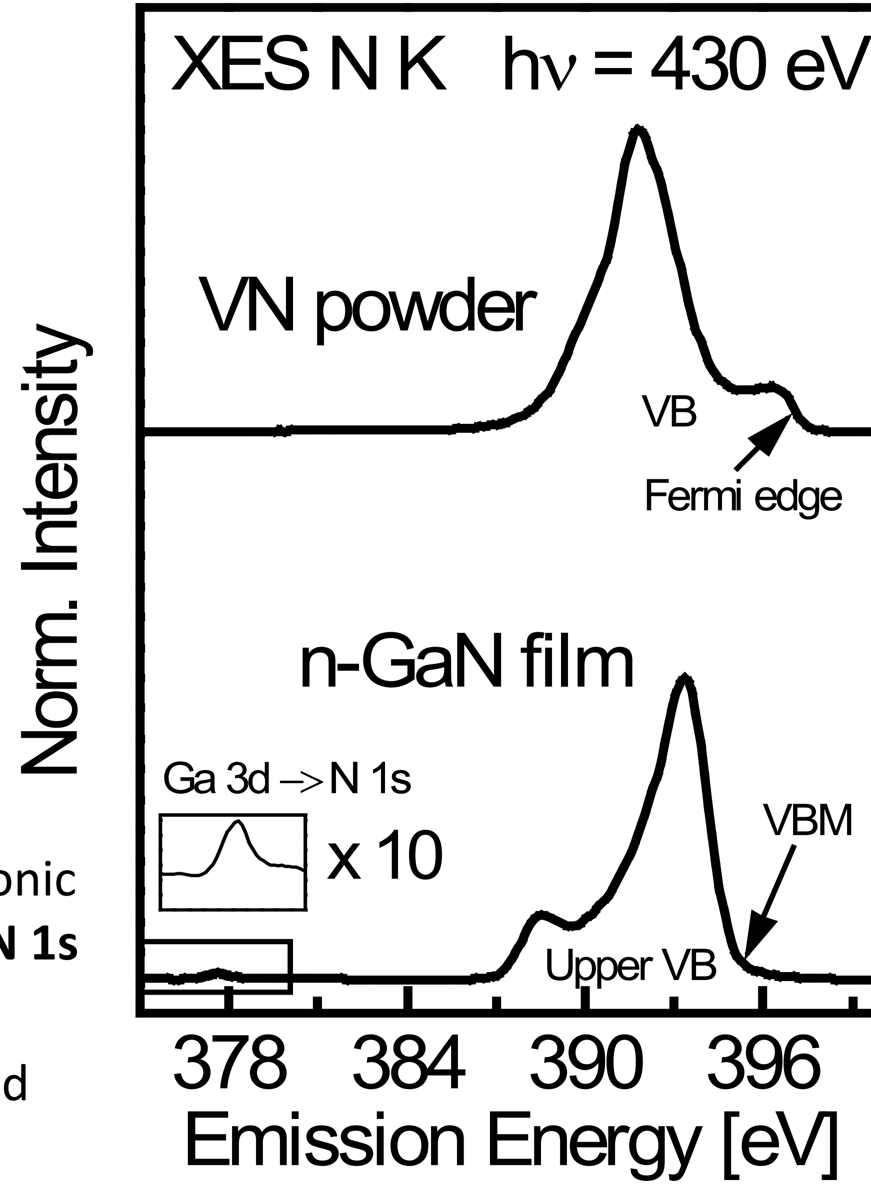




- The implanted N atoms can be detected using N K XES
- N atoms are clearly in a nitride environment
- Clear evidence for N-In and N-Ga bonds

N K XES of InN, GaN, VN



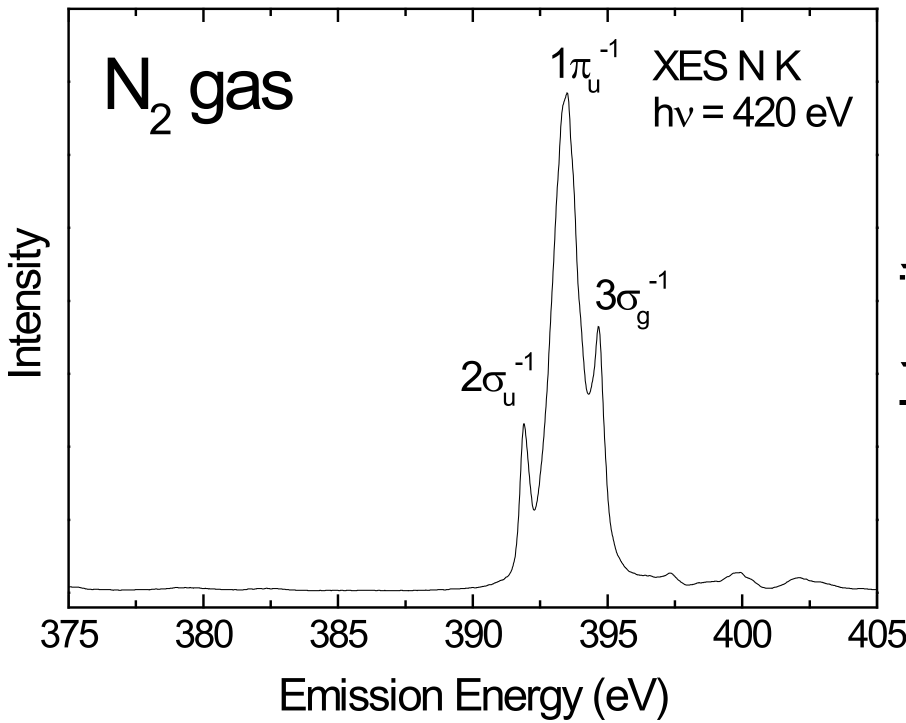


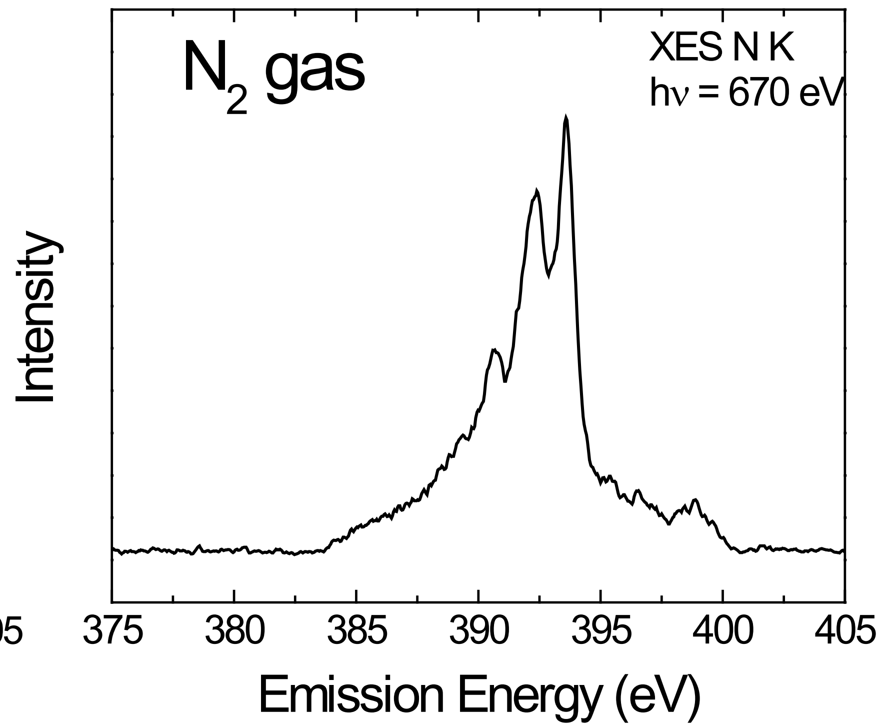
APL **93**, 172106 (2008)

- Spectra give detailed insight into the electronic valence structure **from the viewpoint of a N 1s hole**
- VN spectrum shows Fermi edge (as expected for metallic behavior)
- n-GaN spectrum shows Ga 3d -> N 1s transition at 377.6 eV, shows presence of Ga – N bonds
- InN: In 4d – N 2p states 17 eV below VBM

It's clearly not molecular Nitrogen (gas)!

(Accomplishments)





- Measurements were performed in an *in-situ* gas cell in the SALSA chamber (a similar *in-situ* cell is under construction for liquid/solid PEC interfaces!)

Main Tasks

(Relevance)

1. Determine the benchmark electronic structure of (Ga,In)P_2 surfaces

2. Investigate impact of N-treatment on (Ga,In)P_2 surfaces

3. **Correlate spectroscopy with theory to establish base for predictive capabilities**

Theory-Experiment feedback cycle (see PD058)

(Collaborations)

NREL experiments: (DOE lab)
- H. Wang, T. Deutsch, J. Turner
- DOE H_2 program
- Synthesize electrode materials
- Assemble device
- Analyze H_2 production performance and corrosion resistance

Sample delivery

AIST theory: (METI lab)
- M. Otani
- METI-DOE Clean Energy Technology Action Plan
- International PEC Working Group Member
- *Ab-initio* dynamics of biased systems

Basic information on electrodes

Detailed microscopic information

XAS/XES calculation under bias

Simulation of biased systems

UNLV experiments: (University)
- M. Weir, L. Weinhardt, K. George, C. Heske
- DOE H_2 program
- Hi-fidelity *in-situ* characterization of water-electrode interface using X-ray spectroscopy

X-ray spectroscopy

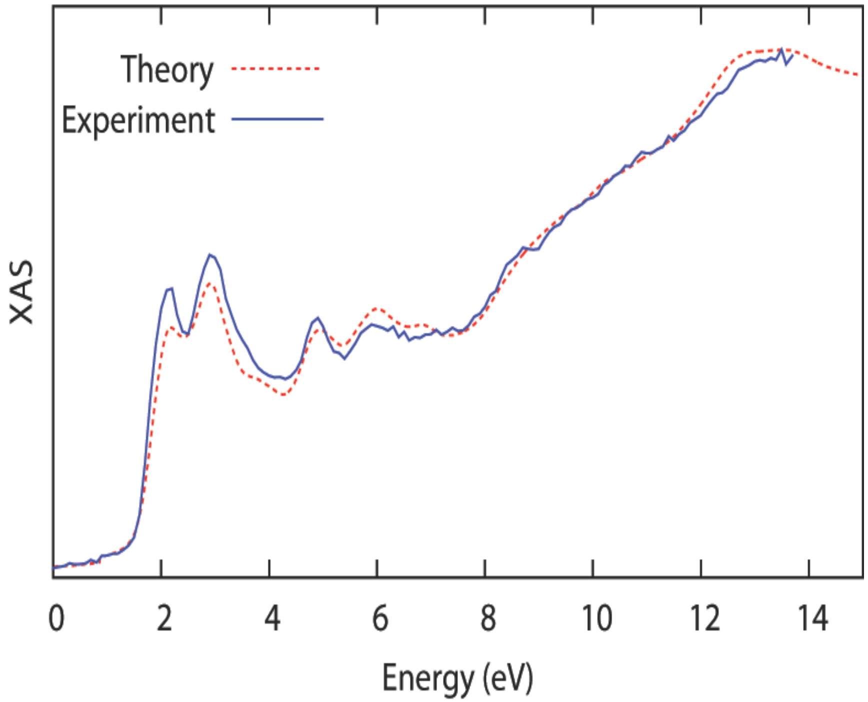
LBNL theory: (DOE lab)
- D. Prendergast
- Molecular Foundry User Grant
- X-ray spectrum simulations

LLNL theory: (DOE lab)
- W. Choi, B. Wood, T. Ogitsu
- DOE H_2 program
- Theoretical description of III-V surfaces and water-electrode interface
- Highly scalable simulations *ab-initio* dynamics

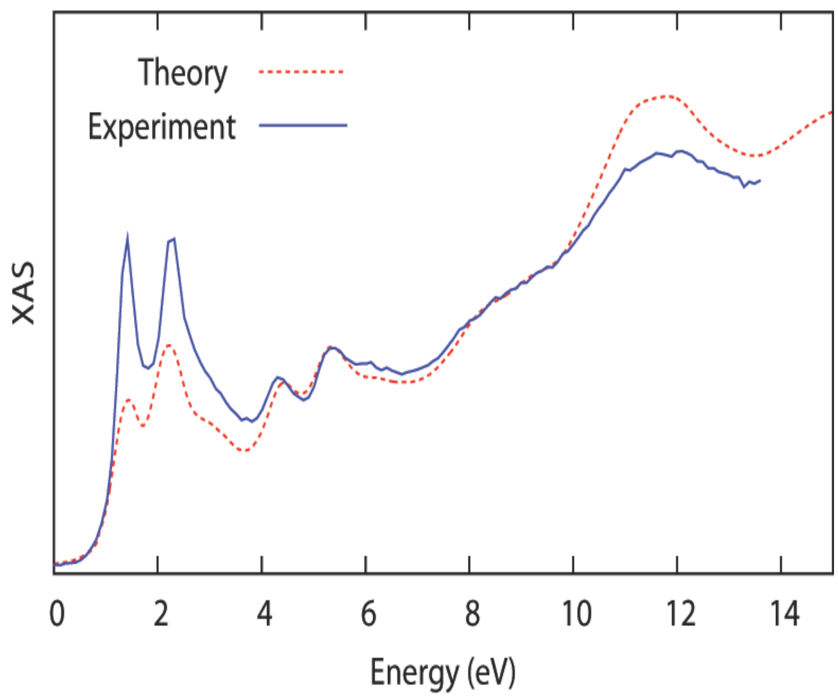
Good agreement of experimental and simulated X-ray Absorption Spectroscopy of GaP and InP (see also PD058) *(Accomplishments)*

Bulk (reference system)

GaP



InP



$(Ga,In)(P,N)_x$ Summary (Accomplishments)

- Ion-treatment series of air-exposed sample gives first insights into electronic structure
- Optimally packed sample gives much cleaner starting material, allowing first look at pristine band edge positions (some surface cleaning under way)
- Detected N in nitrogen-treated samples with enhanced chemical stability – chemical environment of N could be assessed
- Good agreement in GaP and InP XAS between experiment and theory (LLNL)
- *In-situ* gas cell is operational, liquid/solid cell in development

Research Plan & Basis for Continuation of Research

(Proposed Future Work)

- Continue the close collaboration on (Ga,In)(P,N)$_x$ with our partners at NREL and LLNL
- Determine electronic and chemical properties of PEC candidate materials, compare with theory, and answer as many questions as possible
- Study the impact of material modifications by the collaboration partners (in particular surface nitridation)
- Study material durability after exposure to a variety of ambient environments
- Find unexpected things (e.g., guest species)
- Depending on funding availability: further develop cells for *in-situ* soft x-ray studies at the Advanced Light Source (Berkeley Lab)

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, with particular emphasis on $GaInP_2$–based systems from NREL
- Portfolio of experimental techniques ranging from “standard” to “pushing the edge forward” (*in-situ* still on the horizon)
- Requires close collaboration with synthesis group at NREL and theory group at LLNL/Berkeley Lab
- 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