Characterization and Optimization of Photoelectrode Surfaces for Solar-to-chemical Fuel Conversion

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Lawrence Livermore National Laboratory
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Project ID# PD058

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Overview

Timeline

- Start: March 2010
- End: October 2012
- Percent complete: 70%

Project continuation and direction determined annually by DOE

Barriers

- Z. Materials Durability
- Y. Materials Efficiency

Budget

Total project funding
- DOE $340K
- Contractor $420K

(50% of PI, 5% of co-PI, 100% of a PD)

Funding for FY10: $100K
Funding for FY11: $140K
Funding for FY12: $100K

Partners

- DOE EERE PEC Surface Validation WG:

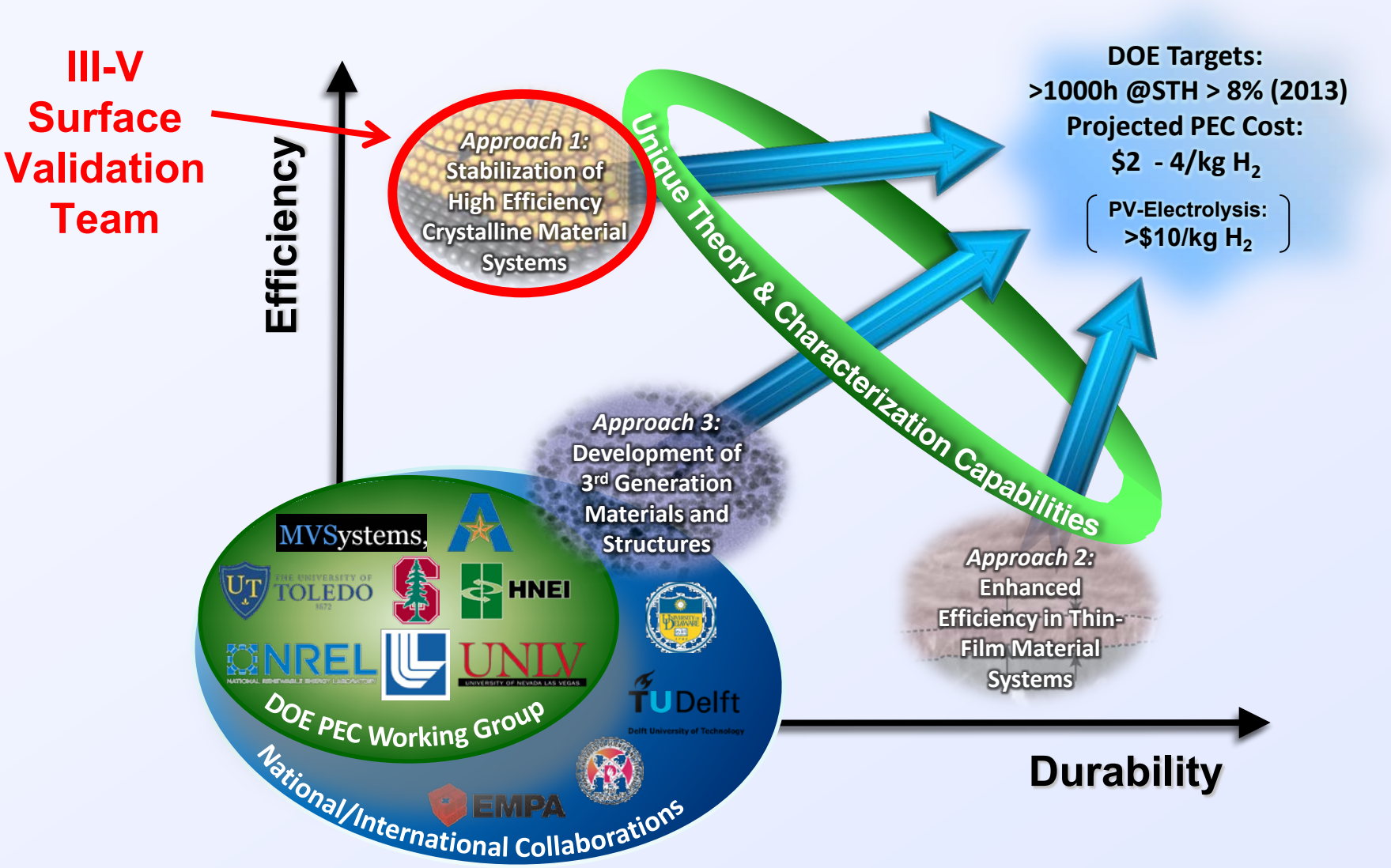
Deutsch/Wang/Turner (NREL)
Heske (UNLV)

- Unfunded partners:

Prendergast (LBNL)
Otani (AIST Japan)

Project lead: T. Ogitsu, LLNL

Photoelectrochemical Hydrogen Working Group

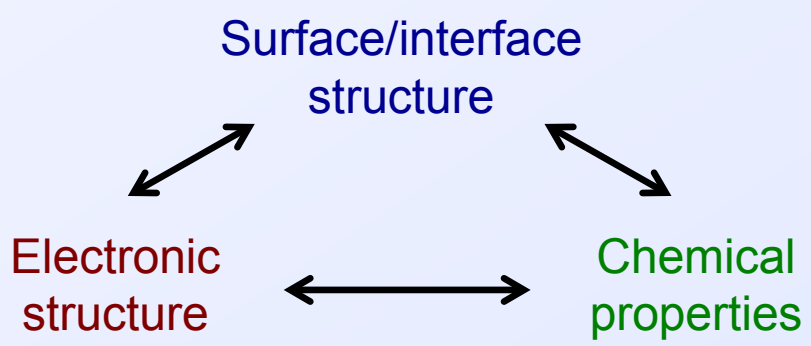


Relevance

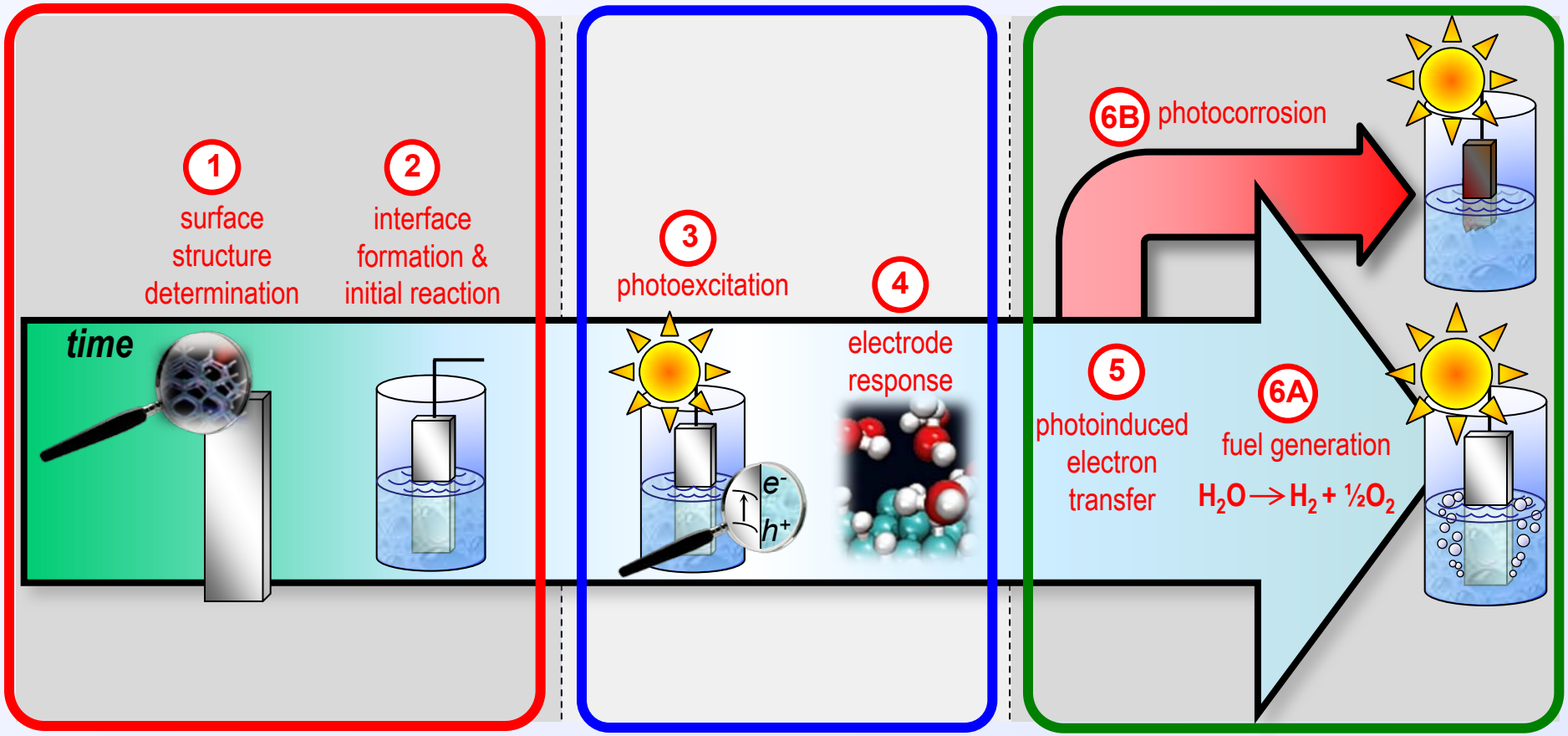
- **Objectives**
  - *Develop **theoretical tool chest** for modeling photoelectrochemical systems*
  - *Compile **publications database** of research on relevant photoelectrode materials*
  - *Uncover key **mechanisms of surface corrosion** of semiconductor photoelectrodes*
  - *Understand **dynamics of water dissociation and hydrogen evolution** at the water-photoelectrode interface*
  - *Evaluate **electronic properties** of the surface and water-electrode interface*
  - *Elucidate relationship between **corrosion and catalysis***
  - *Provide **simulated X-ray spectra** to UNLV for interpretation of experimental results*
  - ***Share research insights** with the PEC WG members*
- **Specific relevance to H_2 program**
  - *Inform experimental efforts to increase **durability** of photocatalyst (Barrier Z)*
  - *Inform experimental efforts to increase **catalytic efficiency** (Barrier Y)*

Approach

- Extract atomistic **structural models** from complex quantum-mechanical simulations of III-V/water interfaces
- Understand origin of **the chemistry of corrosion and water dissociation** at III-V/water interfaces
- Assess implications of key features in the **electronic structure** of III-V/water interfaces
- Use **simulated X-ray spectra** of model surfaces for validation and additional insight from experiments
- Recruit external **collaborators** to extend theoretical tool chest



Stages of the photoelectrochemical reaction



Stage 1: reaction precursors

Stage 2: light absorption

Stage 3: product formation

Technical approach for Stage 1 (primary focus of FY11)

1. Extract **local models** for O/OH-rich InP/GaP(001)
2. **Electronic structure/chemistry** of local models
3. **Build surfaces** based on local models
4. Run *ab initio* dynamics for **structure of interface**
5. Validate against XAS/XES **experiments** by UNLV

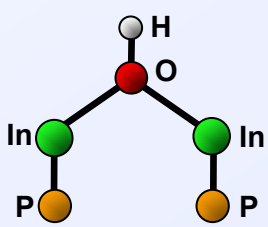
Quantum-Espresso code

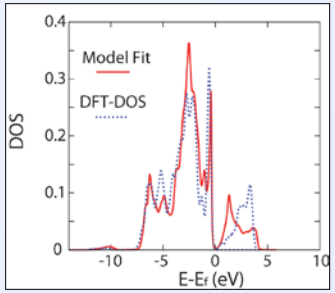
DFT calculations

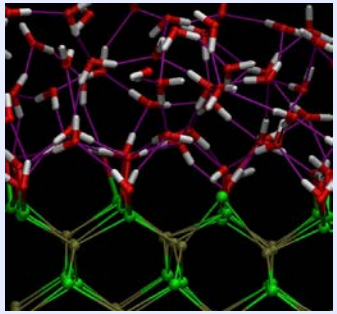
- 9-layer periodic slabs
- PBE-GGA XC functional
- (2 x 4), (2 x 1), (1 x 2) reconstructions

Car-Parrinello dynamics

- 15 ps +5 ps equilibration @ T = 400 K
- Δt = 10 a.u., μ=600 a.u.
- 112 InP/GaP atoms (4 x 4) + 160 D_2O







Milestones and deliverables

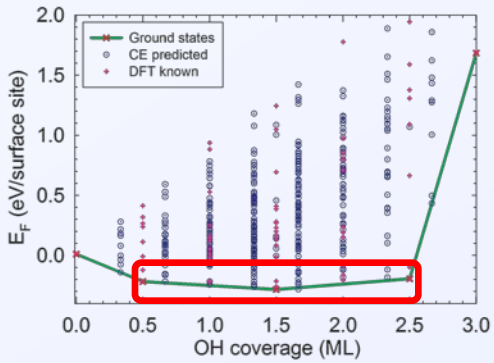
Milestone	Description	% Completed
1	Modeling of clean, O-decorated, and OH-decorated III-V surfaces and electrode-electrolyte interfaces	100
2	Implementation of tools for modeling of surfaces under bias	60*
3	Examine energetics and chemistry of nitrogen incorporation	50
4	Investigate precursor states for surface photocorrosion processes	90
5	Study mechanisms of dissociative adsorption of water as a first step in photo-induced hydrogen evolution	90
6	Deliver simulated spectra of model GaP, InP, and $GaInP_2$ surfaces to experimental III-V characterization team at UNLV	60
7	Modeling of surfaces under bias	10
8	Investigate adsorption and redox chemistry of $GaInP_2$ surfaces and interfaces	30

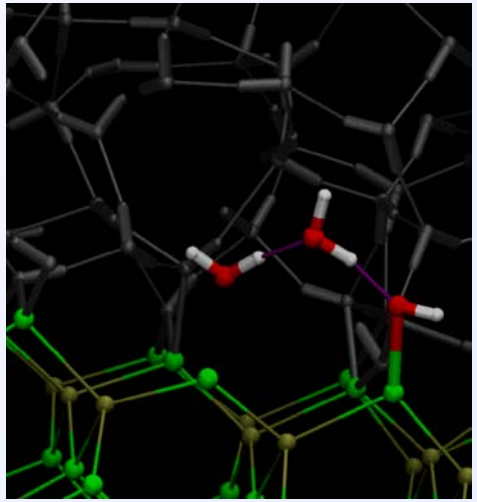
*Implementation in Quantum ESPRESSO completed in FY10; higher-scalability Qbox implementation due in FY12

Summary of previous technical accomplishments

Flat free energy profile for OH-decorated surface:

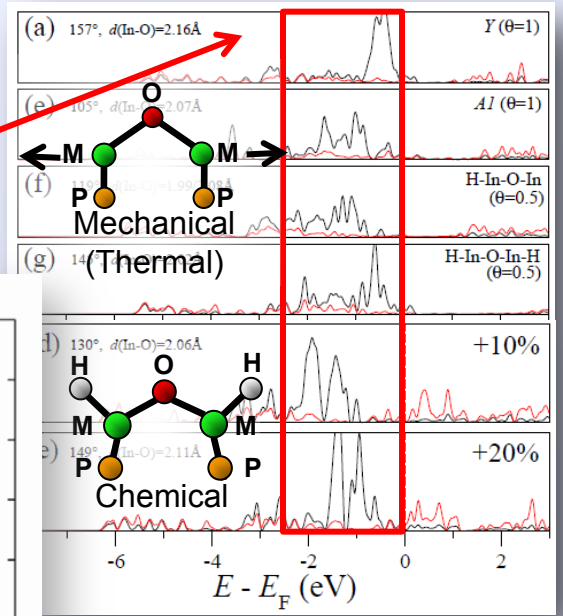
- ✓ Can shuttle protons to charge-transfer sites via H-bond bridges





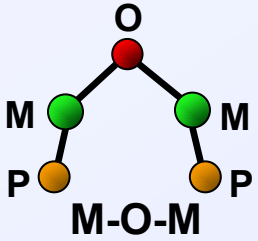
Carrier mobility affected by surface structure

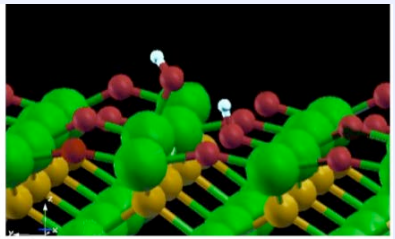
- ✓ Discovery of oxygen-induced hole trap
- ✓ Hole trap can be induced mechanically (strain) or chemically (edge bonding)
- ✓ Possible relevance to corrosion?

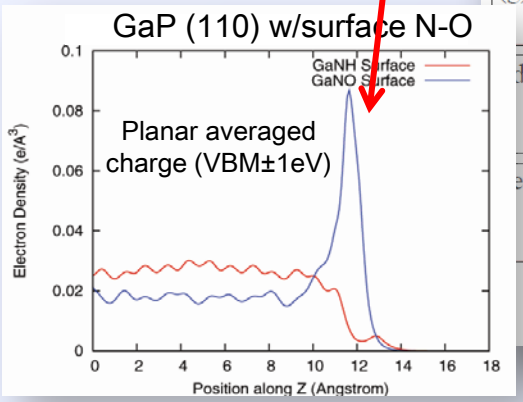


Oxygen needed for H_2O splitting

- ✓ Connection to known oxide catalysts?



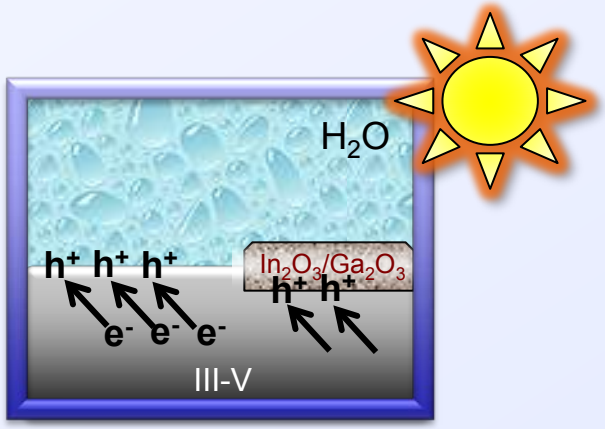


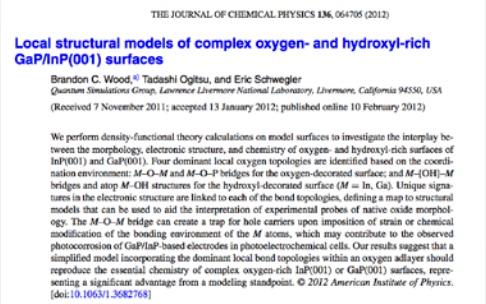


Overview of new technical accomplishments

Project has met all target milestones

- Expanded literature search to understand science of III-V oxides (idea of oxygen relevance dates to 1980s)
- Published summary on surface morphology and electronic structure of oxygen- and hydroxyl-rich III-V
- Experimental evidence supporting proposed hole trapping corrosion mechanism was realized through team discussions
- A simple model to describe charge transfer reaction was developed and applied to the Volmer reaction on $GaInP_2(001)$
- Calculated and compared X-ray absorption spectra with experiments (partnership with UNLV and LBNL)





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Local structural models of complex oxygen- and hydroxyl-rich GaP/InP(001) surfaces

Brandon C. Wood,[a)] Tadashi Ogitsu, and Eric Schwegler
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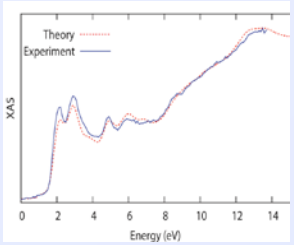
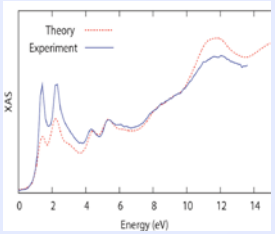
(Received 7 November 2011; accepted 13 January 2012; published online 10 February 2012)

We perform density-functional theory calculations on model surfaces to investigate the interplay between the morphology, electronic structure, and chemistry of oxygen- and hydroxyl-rich surfaces of InP(001) and GaP(001). Four dominant local oxygen topologies are identified based on the coordination environment: *M*–O–*M* and *M*–O–P bridges for the oxygen-decorated surface; and *M*–[OH]–*M* bridges and atop *M*–OH structures for the hydroxyl-decorated surface (*M* = In, Ga). Unique signatures in the electronic structure are linked to each of the bond topologies, defining a map to structural models that can be used to aid the interpretation of experimental probes of native oxide morphology. The *M*–O–*M* bridge can create a trap for hole carriers upon imposition of strain or chemical modification of the bonding environment of the *M* atoms, which may contribute to the observed photocorrosion of GaP/InP based electrodes in photoelectrochemical cells. Our results suggest that a simplified model incorporating the dominant local bond topologies within an oxygen adlayer should reproduce the essential chemistry of complex oxygen-rich InP(001) or GaP(001) surfaces, representing a significant advantage from a modeling standpoint. © *2012 American Institute of Physics*. [doi:10.1063/1.3682768]

GaP **InP**





Technical accomplishment: Database of PEC research
(in progress)

- Approximately 800 papers (1960-present) have been collected, indexed, and stored as of March 2012
- Information on relevant papers is shared among team members using online collaboration tools
- Expanded detailed review on surface and interfacial properties of $GaInP_2$ (99 papers total)
  - Actively investigating on correlation between CuPt ordering, surface morphology and electronic structure/carrier lifetime
- Further extending review to surface and interfacial properties of native oxides of III-V semiconductors

Technical accomplishment: FY11 surface oxide/hydroxyl study

Completed and published in Journal of Chemical Physics

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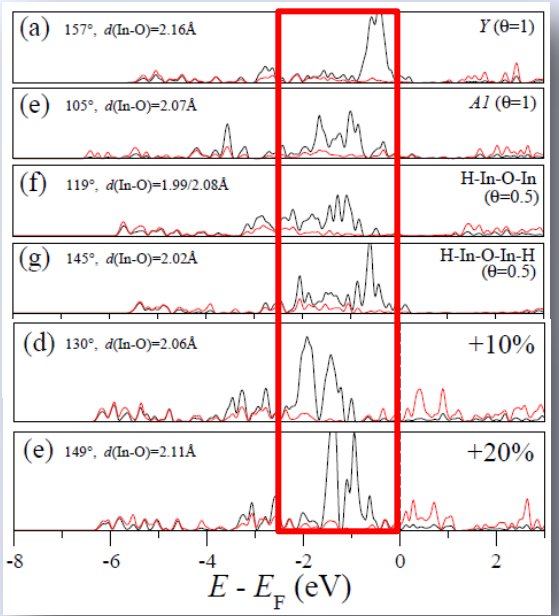
Technical accomplishment: Indirect evidence for our proposed corrosion mechanism based on team discussions

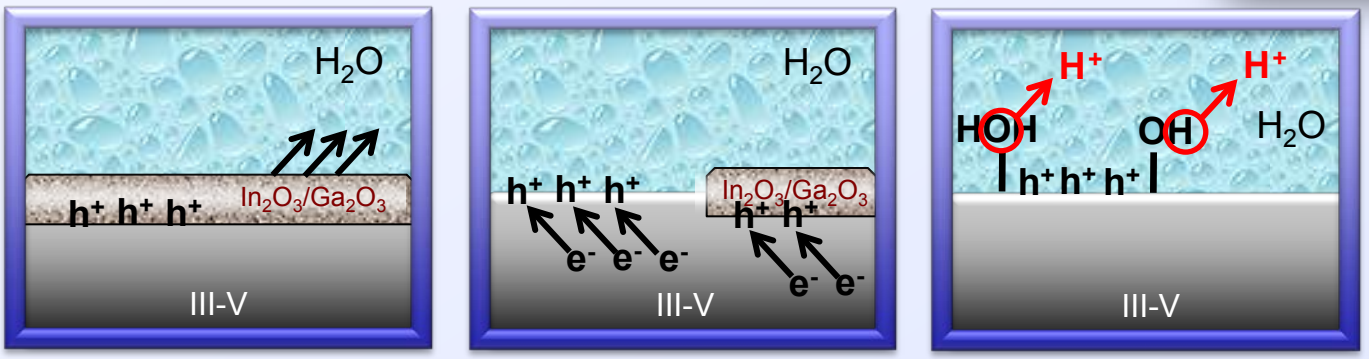
A re-evaluation of past NREL experiments on $GaInP_2$ [Deutsch, Koval, Turner, J. Phys. Chem. B 110, 25297(2006)] supported the hole trapping corrosion scenario we proposed in FY11. There, corrosion was specifically linked to photoexciton generation, which uniquely creates hole carriers, rather than application of external bias.

Confirmation and more detailed understanding expected from *in situ* XAS/XES (currently in progress)

Hole traps found in oxygen-rich GaP/InP (FY11)

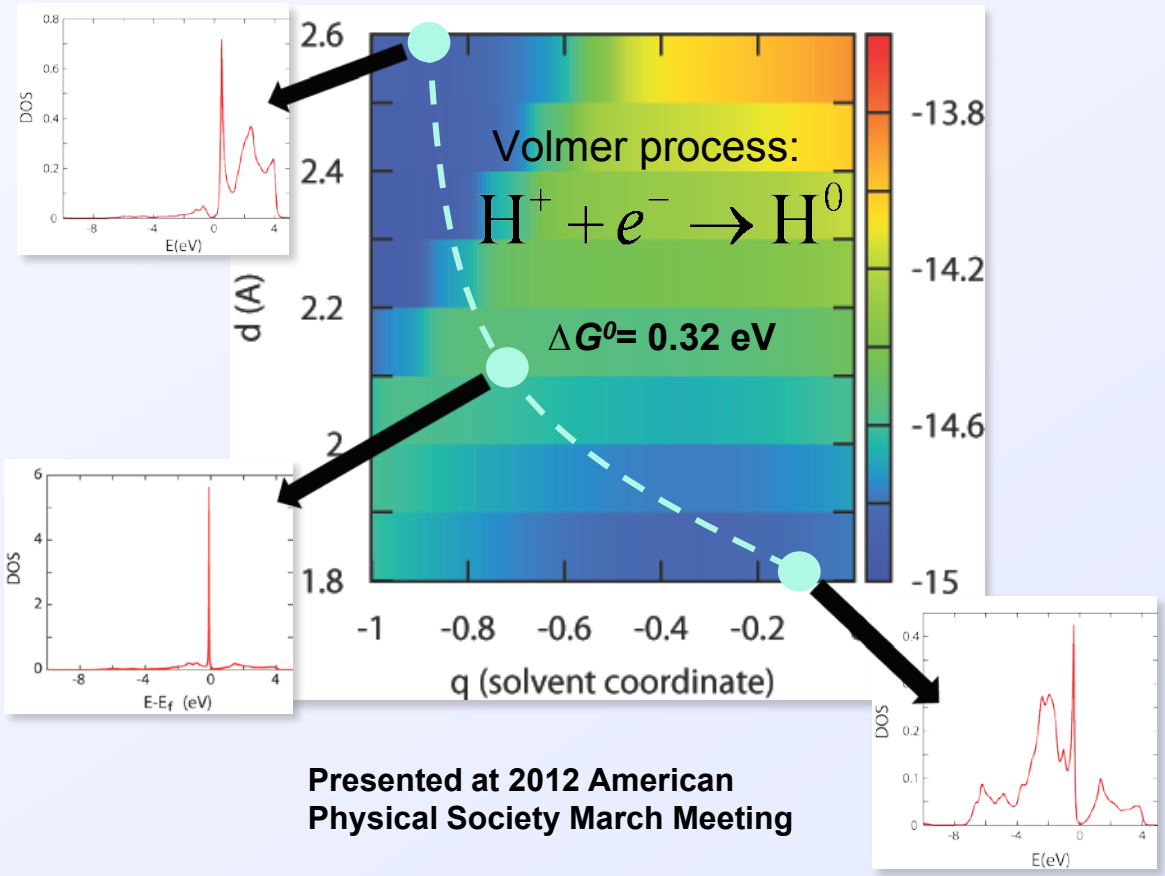


Three possible hole-trapping corrosion mechanisms



Technical accomplishment: Identified origin of high barrier for Volmer process of Stage 3 HER on $GaInP_2$ (001)

Simplified model uses input from quantum mechanics to estimate free energy barriers for Stage 3 hydrogen evolution reaction (HER)



Presented at 2012 American Physical Society March Meeting

- High barrier due to lack of states near E_F (no interaction)
- Method can be used for efficient screening of candidate surface treatments for enhanced catalytic activity

- Method based on Santos *et al.*, Phys. Rev. B **79**, 235436 (2009)
- Chemisorption (Anderson-Newns)
- Proton solvation & charge transfer (Marcus-Hush)
- Density of states (quantum-mechanical calculations)

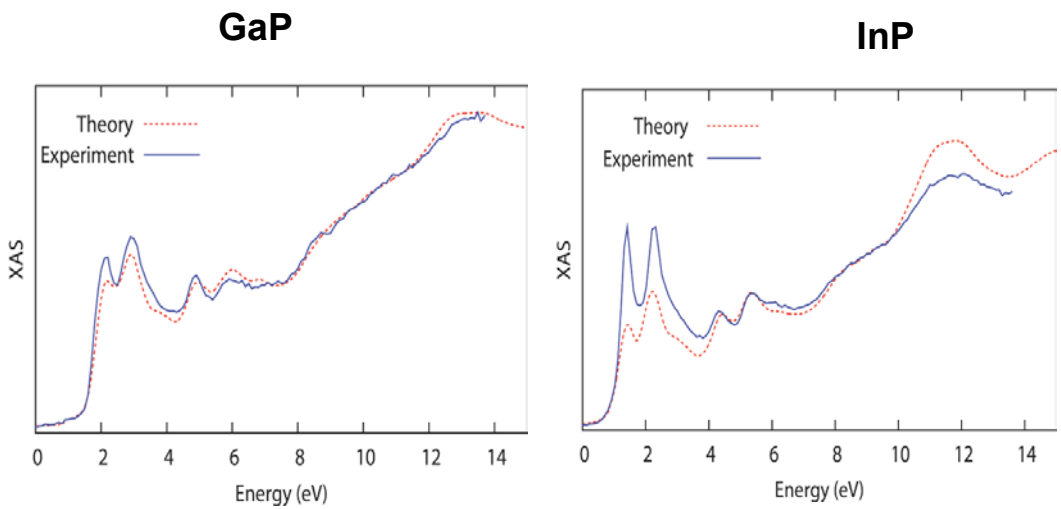
Materials characterization via X-ray spectroscopy

- **Theory/experiment collaboration**
  - *Construct model surfaces based on local topologies developed in FY11 for comparison of simulated and calculated X-ray spectra*
  - *Permits confirmation of relevant surface states and corrosion pathways*
  - *Theoretical site-dependent spectra can aid experimental interpretation*
- **Experiment side:**
  - *Samples provided by T. Deutsch (NREL) and delivered via controlled scheme established through team discussions*
  - *Detailed characterization performed by M. Weir, L. Weinhardt, K. George, and C. Heske (UNLV) using Advanced Light Source (LBNL)*
- **Theory side:**
  - *XAS calculations and analysis performed by W. Choi & T. Ogitsu (LLNL)*
  - *Development and support for theoretical ab-initio X-ray absorption/emission spectrum code via Molecular Foundry User Project with D. Prendergast (LBNL)*
  - *Integration of X-ray spectroscopy code into a common software package to permit XAS simulation under bias voltage. Performed by B. Wood (LLNL) and D. Prendergast (LBNL).*

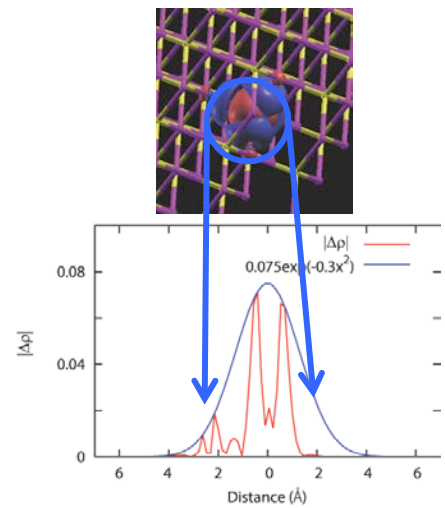
Technical accomplishment: Simulated XAS of GaP, InP, $GaInP_2$

- Established calculation procedure for P-L2,3 edge XAS of GaP, InP, $GaInP_2$
- Experimental (UNLV) and theoretical (LLNL) bulk spectra show excellent agreement
- Completed selection and preparation of local topologies for III-V surface XAS calculation

Bulk (reference system)



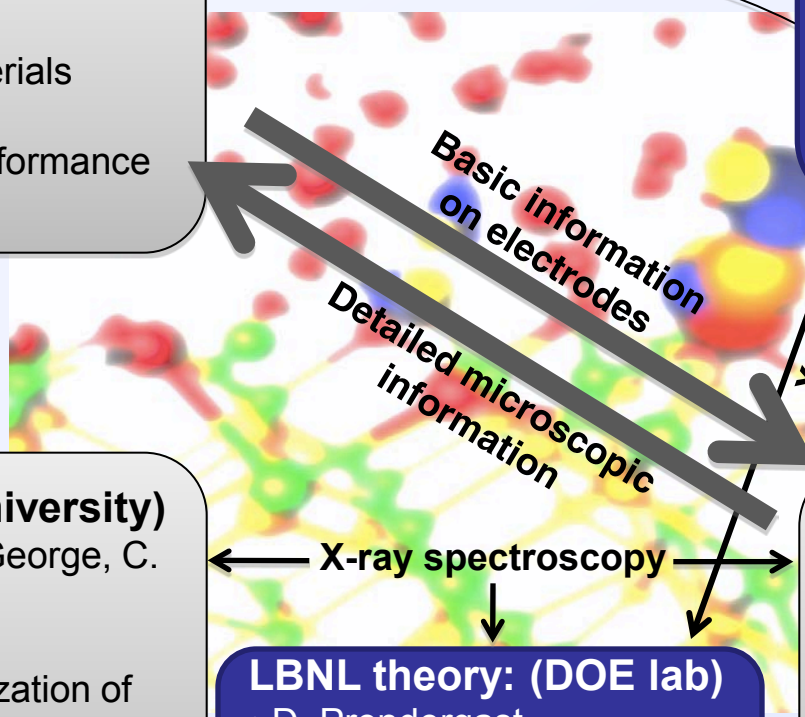
Exciton size assessed



Collaborations: Theory-experiment feedback cycle

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

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

Sample delivery

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

Proposed future work

Milestone	Description	% Completed
1	Highly scalable software implementation for higher-throughput modeling of surfaces under bias	0
2	Examine energetics and chemistry of nitrogen incorporation	50
3	Study mechanisms of the Stage 3 hydrogen evolution reaction and related corrosion processes	20
4	Deliver simulated spectra of model GaP, InP, and $GaInP_2$ surfaces to experimental III-V characterization team at UNLV	60
5	Static modeling of surfaces under bias	10
6	Investigate adsorption and redox chemistry of $GaInP_2$ surfaces and interfaces	30
7	Dynamics of clean, O-decorated, and OH-decorated III-V electrode-electrolyte interfaces under bias	0

Summary

- Compiled, reviewed, and shared available information on III-V electrode materials (ongoing)
- Simulation results on native oxide and hydroxyl on III-V surfaces published in J. Chem. Phys.
- Team discussion and re-examination of experiments on $GaInP_2(001)$ provided indirect support of proposed hole trap corrosion mechanism
- Adopted model calculation method for examining the hydrogen evolution reaction on $GaInP_2(001)$
- Continued joint theoretical/experimental study on III-V electrode surfaces (continue through FY12)

Technical backup slide: Details of electron-transfer model

$$\rho_a(\varepsilon) = \frac{1}{\pi} \frac{\Delta(\varepsilon)}{\{\varepsilon - [\varepsilon_a + \Lambda(\varepsilon) - 2\lambda q]\}^2 + \{\Delta(\varepsilon)\}^2}$$

ε_a : Hydrogen level

Δ : Level broadening

Λ : Level shift by chemisorption

$2\lambda q$: Level shift by solvent fluctuation

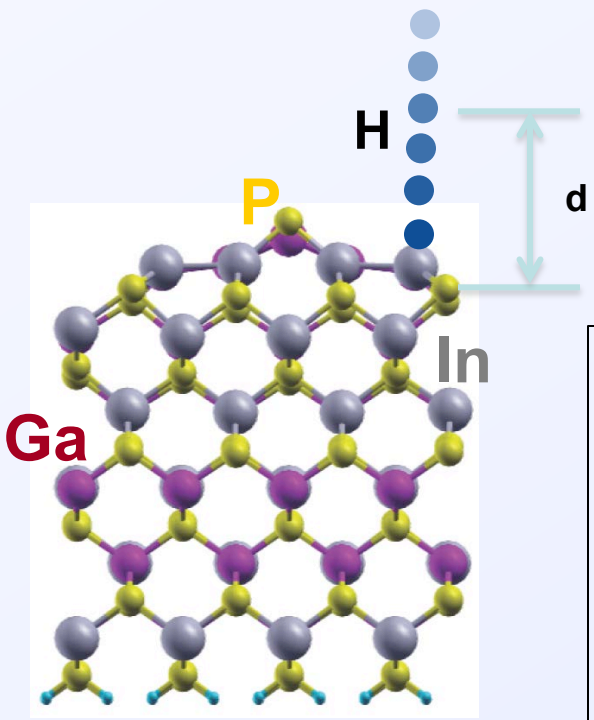
q : Solvent coordinate

λ : Reorganization energy

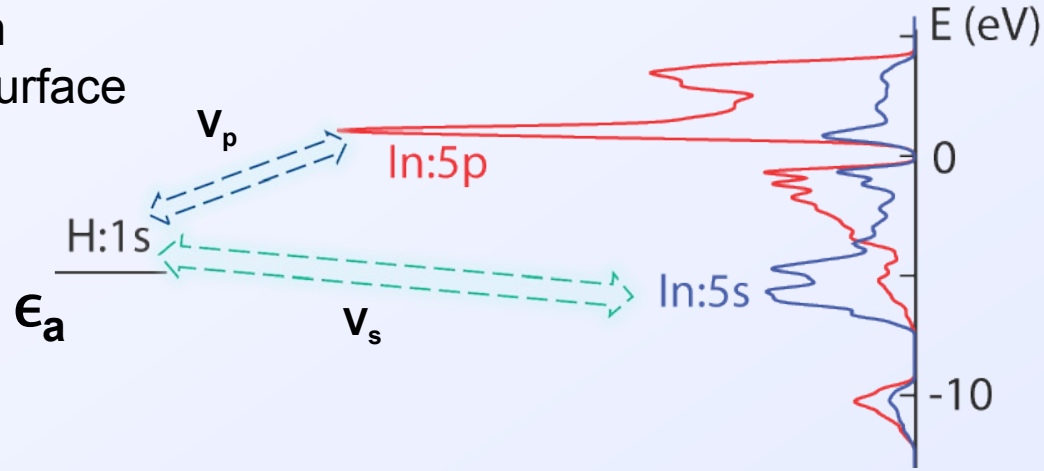
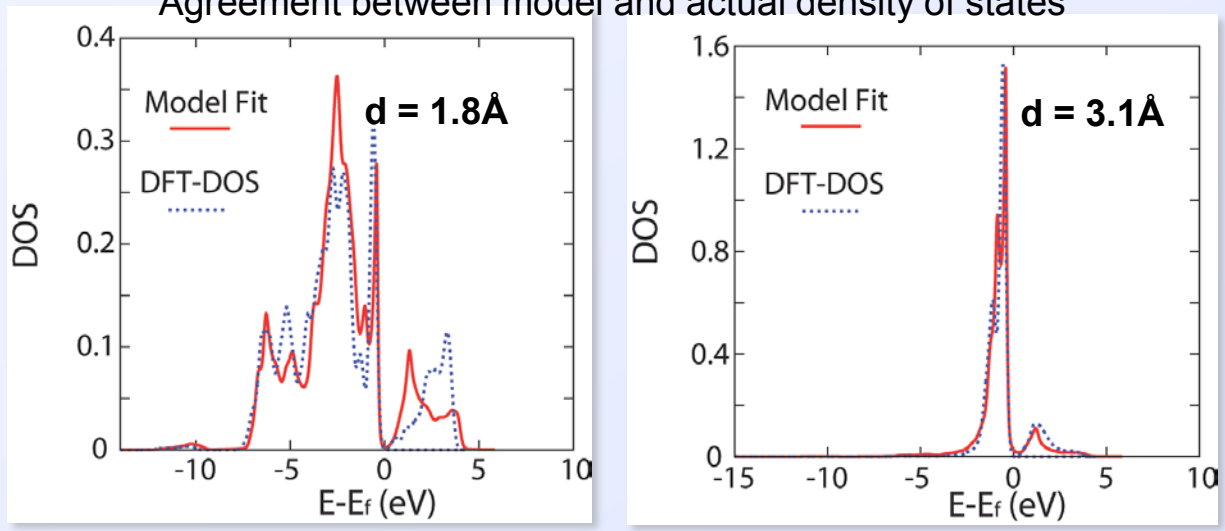
$$E(q) = \int_{-\infty}^{0} \rho_a(\varepsilon)\varepsilon d\varepsilon + \lambda q^2 + 2\lambda q$$

Technical backup slide: Application of model to $GaInP_2$

Electronic structure of hydrogen changes as it approaches the surface



$GaInP_2$(001)
a(2X4) surface
CuPt phase



Agreement between model and actual density of states