# 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 2013
- Percent complete: 70%

**Project continuation and direction determined annually by DOE**

## Task 5 Barriers

- AE. Materials Efficiency
- AF. Materials Durability

## Budget

Total project funding
- DOE $405K
- Contractor $690K

(30% of PI, 5% of co-PI, 100% of a PD)

Funding for FY10: $100K
Funding for FY11: $140K
Funding for FY12: $100K
Funding for FY13: $65K

## Partners

- DOE EERE PEC Surface Validation WG:

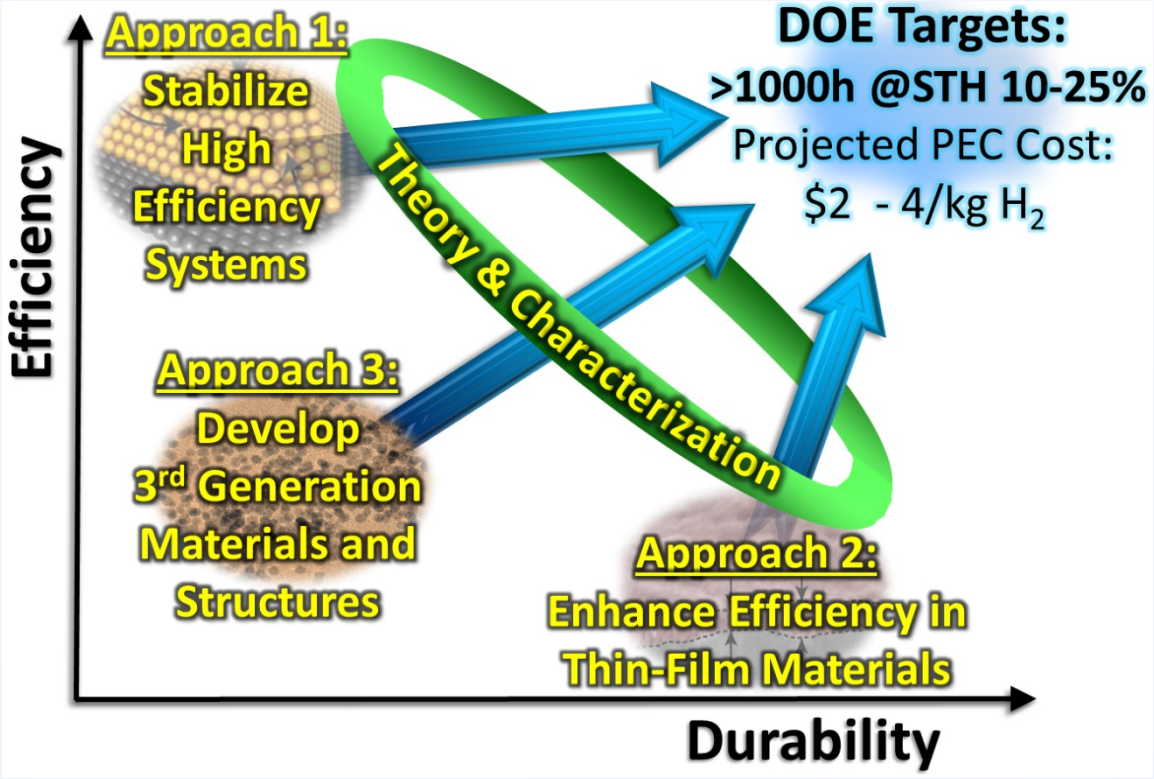
Deutsch/Wang/Turner (NREL)
Heske (UNLV)

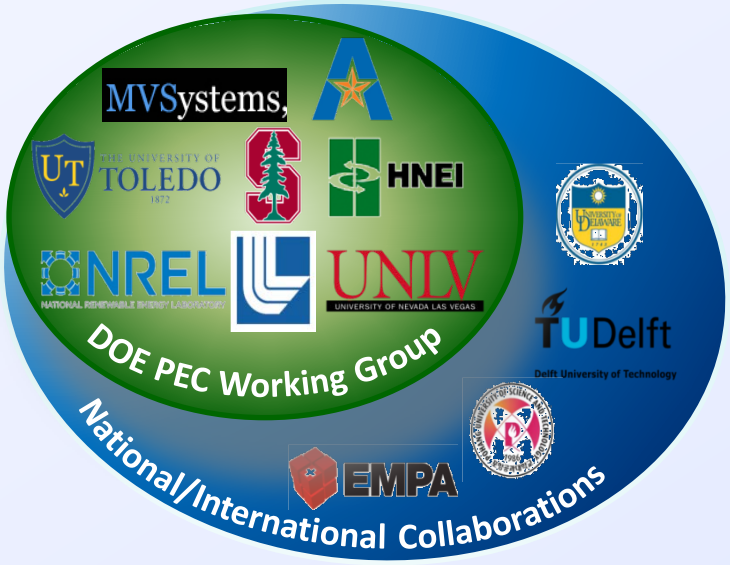
- Unfunded partners:

Prendergast (LBNL)
Otani (AIST Japan)

Project lead: T. Ogitsu, LLNL

# PEC $H_2$ Production Work Group




LLNL (theory) together with UNLV (characterization) works on identification of fundamental properties of electrode & interface relevant for $H_2$ production/corrosion, and share the obtained knowledge with PEC $H_2$ production WG

# Relevance

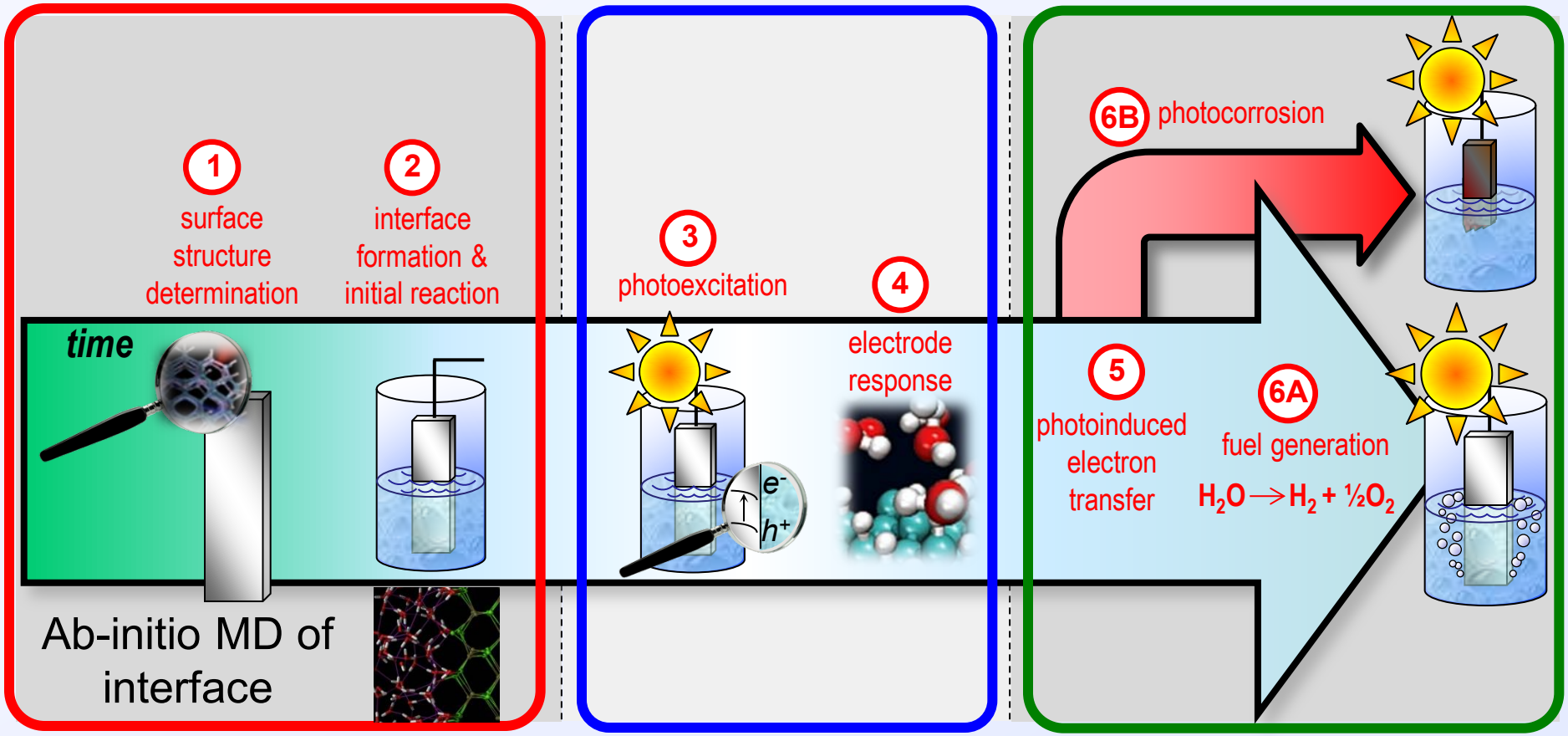
- **Objectives**
  - *Develop **theoretical tool chest** for modeling photoelectrochemical systems*
  - *Compile **publications database** of research on relevant photoelectrode materials*
  - *Uncover key **mechanisms of surface corrosion** of semiconductor photoelectrodes*
  - *Understand **dynamics 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 (Task 5)**
  - *Inform experimental efforts to increase **Materials Efficiency** (Barrier AE)*
  - *Inform experimental efforts to increase **Materials Durability** (Barrier AF)*

# Approach

- Overview: understand relationship between the microscopic property of the electrode-electrolyte interface and the device performance using ab-initio DFT simulations and X-ray spectroscopy
  - Investigate on the microscopic mechanisms of the chemistry of corrosion and water dissociation at electrode/electrolyte interfaces using ab-initio molecular dynamics simulation method
  - Investigate on the microscopic electrode stabilization mechanism due to $N^{2}+$ bombardment treatment developed by T. Deutsch of NREL
    - Investigate on the chemical environment of nitrogen based on measured N K-edge XES of the N treated $GaInP_2$ (NREL/UNLV) and simulated X-ray spectra (LLNL/LBNL)
  - Recruit external collaborators to extend theoretical tool chest
    - A new collaboration with Eva Zurek of Buffalo U on exploring a possibility of developing an intelligent global phase space search
  - Expand our survey to the other materials (eg. CIGS)
    - Development of more universal basic knowledge on PEC electrode materials

*Collect and disseminate basic knowledge relevant for advancing PEC hydrogen production technology*

# Stages of the photoelectrochemical reaction




Stage 1: reaction precursors

Stage 2: light absorption

Stage 3: product formation

# Milestones and deliverables

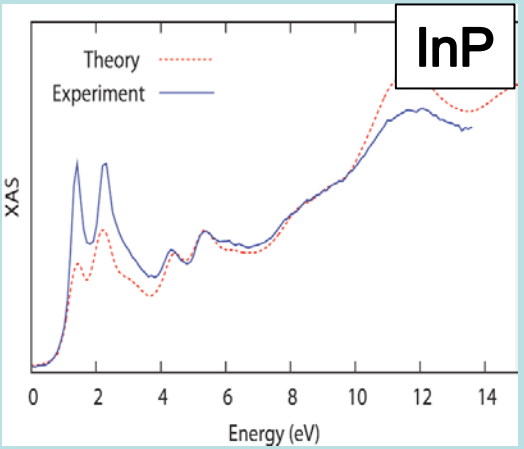
| Milestone | Description | % Completed |
|---|---|---|
| 1 | Summary on the ab-initio MD simulations of III-V/water interface | 90 |
| 2 | Implementation of tools for modeling of surfaces under bias | 80* |
| 3 | Establish calculation procedure for N K edge XES of nitrogen in various chemical environment (assessment) | 90 |
| 4 | Identify the nitrogen impurity states in $GaInP_2$ using simulated/measured N K-edge XES of $GaInP_2$/N | 70 |
| 5 | Investigate on the microscopic mechanisms of $GaInP_2$ electrode stabilization mechanism due to $N_2^+$ bombardment | 30 |
| 6 | Review published works on the properties of CIGS | 20 |

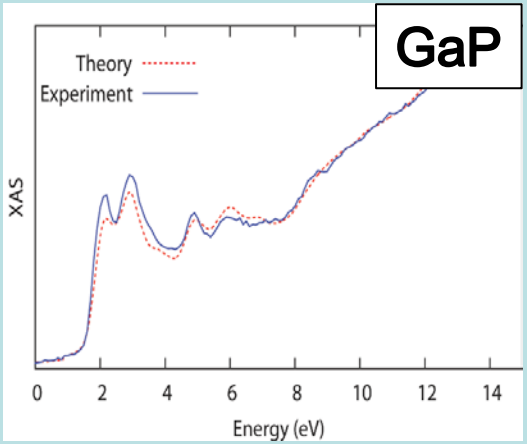
*Implementation in Quantum ESPRESSO completed in FY10; higher-scalability Qbox implementation underway

# Summary of previous accomplishments

- Study on GaP(001)/InP(001) surfaces, oxide/hydroxyl formation was summarized and published [Wood, Ogitsu, Schwegler, JCP **136**, 064705 (2012)]
  - Local model to describe complex surface structure was established, which can be used to interpret (in-situ) X-ray spectroscopy
- Tested a simple model to describe proton adsorption process (Volmer process) in order to accelerate catalyst screening
  - Presence/absence of adsorption barrier and its origin could be determined
- Hole trap corrosion mechanism was proposed and the experimental evidence was found [Deutsch, Koval, Turner, JPC B **110**, 25297(2006)]
- Calculation procedure for P $L_{2,3}$-edge XAS was established and compared against the UNLV experimental results

**P $L_{2,3}$-edge XAS: Theory (LLNL)/ Exp. (UNLV) comparison**



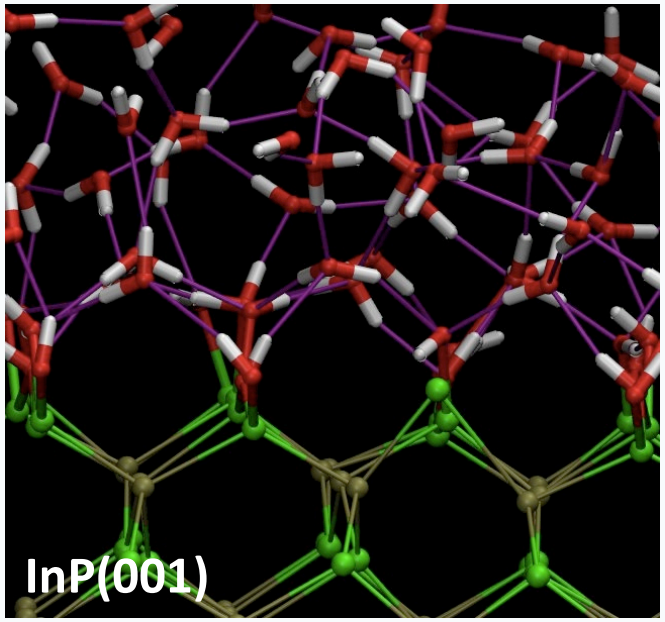



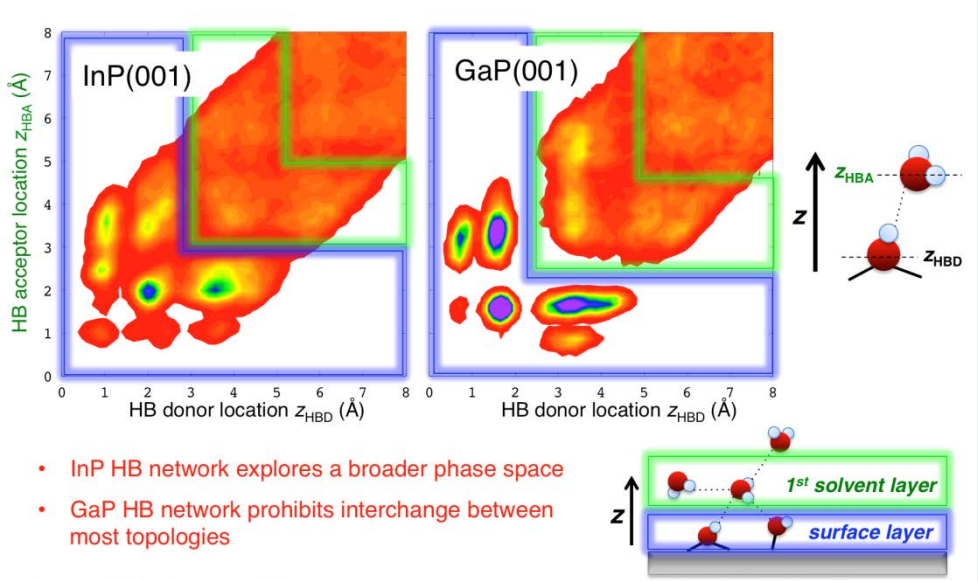
# Technical accomplishment: Database of PEC research
(in progress)

- Approximately 1200 papers (1960-present) have been collected, indexed, and stored as of March 2013
- Information on relevant papers is shared among team members using online collaboration tools
- The detailed literature search on the surface morphology of $GaInP_2$, UNLV experimental results as well as the team discussions led to an identification of a possible cause of an electrode performance issue
  - Deep facet formation and/or possibly partial segregation
  - The deep facet formation has been observed on the thick $GaInP_2$ layer (tandem cell configuration tend to have thick $GaInP_2$ layer)
  - This issue is now under investigation by H. Doscher of NREL
- Further extending review to the other materials such as CIGS and to the computational methods (theory of X-ray spectroscopy, global phase space search method)

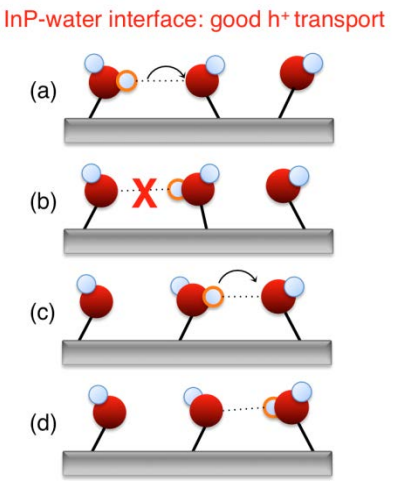
# Technical accomplishment: contrasting $h^+$ transport at water-InP and at water-GaP

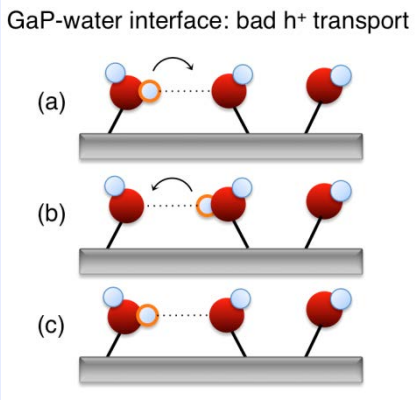
Ab-initio molecular dynamics simulations of water-InP and water-GaP interfaces




- InP HB network explores a broader phase space
- GaP HB network prohibits interchange between most topologies




Experimental observation: Pt loading on GaP(001) improves the conversion efficiency ***only a little*** [ChemPhysChem **13**, 3053 (2012)]

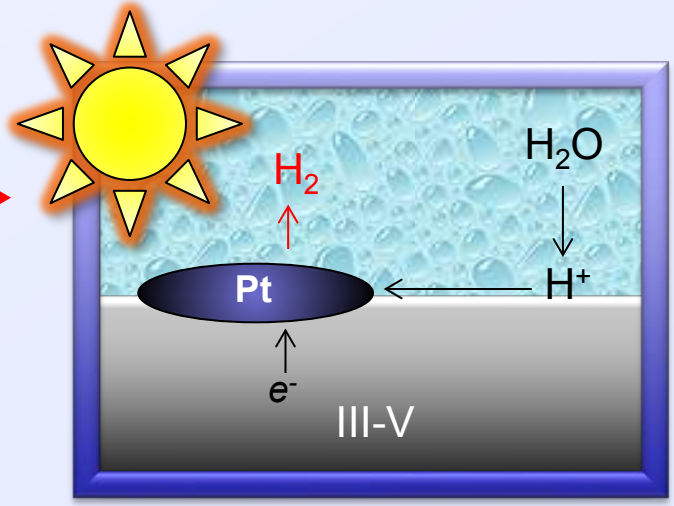
# Implication #1: good PEC electrode needs good $h^+$ transport

Catalyst is added to enhance $H_2$ evolution, but what does the rest of surface do?

- Good surface proton transfer could help collecting and sending protons to Pt co-catalyts
- Evidences: Pt loading does not improve $H_2$ evolution on GaP,[1] while it does on InP

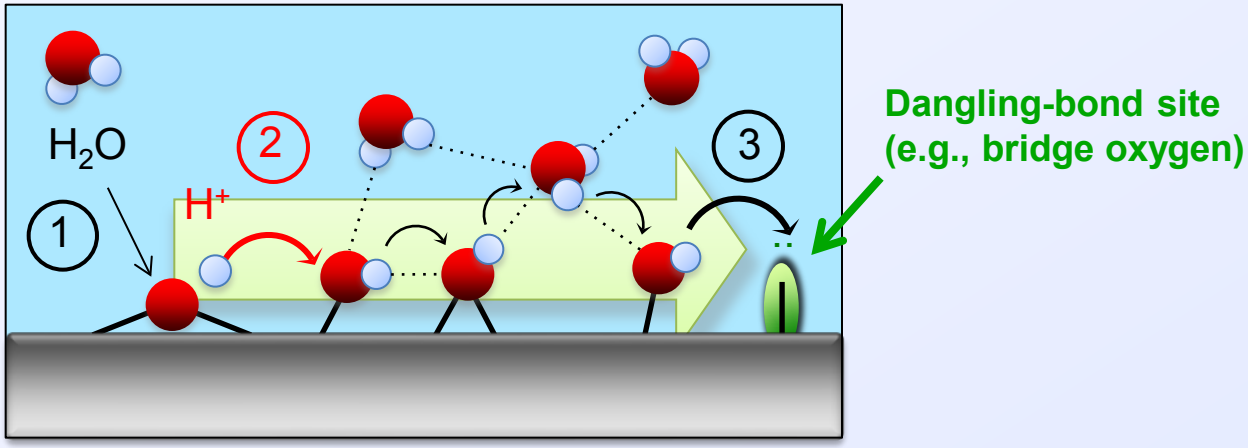
1. Kaiser et al. Chem. Phys. Chem. 13, 3053 (2012)

Catalyst acts as a current collector to improve electron transfer and aid $H_2$ formation, and the rest of surface might be enhancing $H_2$ formation rate by collecting and sending more protons to Pt



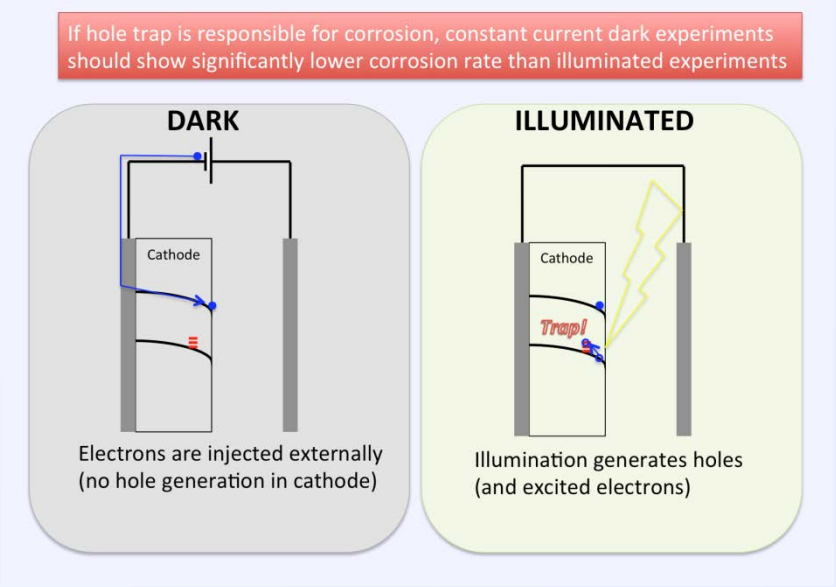
# Implication #2: good $h^+$ transport might improve surface stability

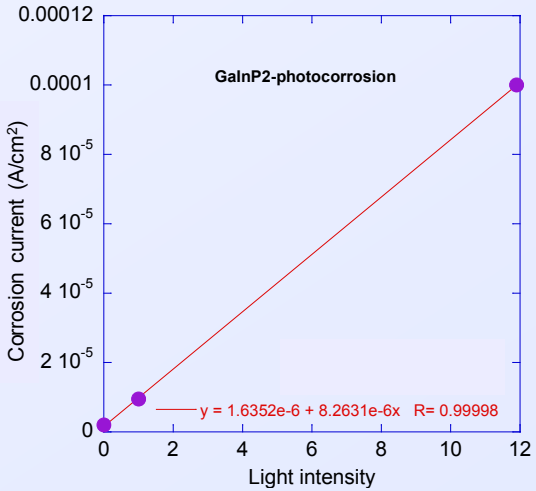
- InP: Long-range surface proton transport means distant dangling bonds can be passivated and charge redistributed across surface
- Can act as self-healing mechanism for surface dangling bonds



# Technical accomplishment: identification of corrosion mechanisms step forward

- FY11: LLNL proposed the hole-trap corrosion mechanism of oxygen rich GaP/InP surface
  - Wood, Ogitsu, Schwegler JCP **136**, 064705 (2012)
- FY12: NREL found the existence of supporting evidence
  - Deutsch, Koval, Turner, JPC B **110**, 25297(2006)
- FY13: H. Wang (NREL) performed additional experiments to confirm that the corrosion rate is linear to the light intensity

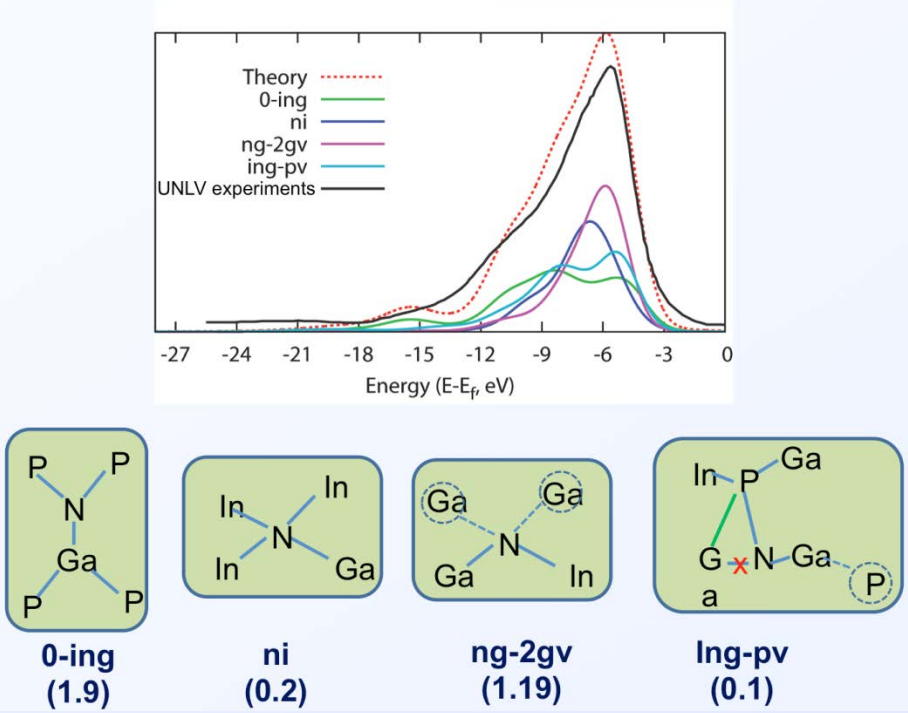



Corrosion current estimated from the Ga concentration in the electrolytes by Wang (NREL)

# Interpretation of N K-edge XES of nitrogen treated $GaInP_2$ (WIP)

- Calculation procedure established
  - Broadening parameters
  - Core-level shift
  - Rational way to deduce the N-environment based on atomic orbital
  - Accurate calibration to experiments using the reference systems (GaN/InN) underway

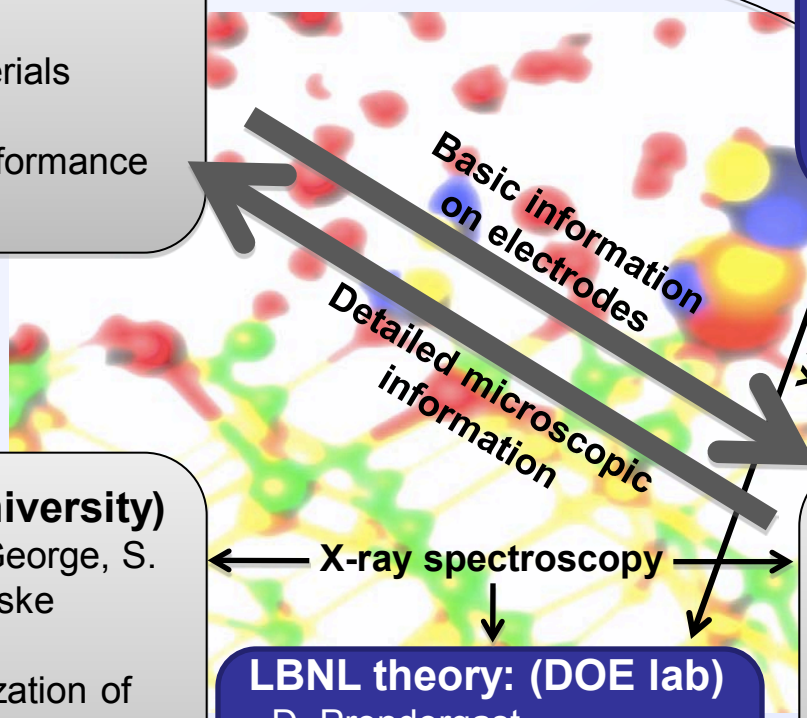



See technical backups for detail

# 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




**UNLV experiments: (University)**
- M. Weir, L. Weinhardt, K. George, S. Alxander, H. Doscher, C. Heske
- DOE $H_2$ program
- Hi-fidelity *in-situ* characterization of water-electrode interface using 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 | Establish theory/experiment self-consistent material characterization scheme using X-ray spectroscopy with UNLV (the scheme applicable to arbitrary system) | 80 |
| 2 | Characterize the chemical environment of nitrogen in $GaInP_2$ based on theoretical/experimental X-ray spectrum (in collaboration with UNLV) | 80 |
| 3 | Disseminate obtained knowledge on the nature of hydrogen bond network at the III-V electrode-electrolyte interfaces | 80 |
| 4 | Investigate on the surface/bulk/interfacial properties of CIGS | 20 |
| 5 | Study mechanisms of the hydrogen evolution reaction and related corrosion processes | 30 |
| 6 | Dynamical modeling of interfaces under bias | 10 |

# Summary

- Compiled, reviewed, and shared available information on III-V electrode materials, theory of X-ray spectroscopy, CIGS (ongoing)
- Ab-initio simulation results on water/III-V interface paper submitted
  - Peculiar difference on H-bond network between $GaP/H_2O$ and $InP/H_2O$
- Work on developing ab-initio derived model to describe catalytic reaction is summarized and ready to submit.
- Continued joint theoretical/experimental study on III-V electrode surfaces (continue through FY13)
  - Identification of N-environments in N treated $GaInP_2$ close to completion
- Initiated a collaboration on CIGS electrode material with U Hawaii and UT Arlington

# Technical backup slide 1: Ab-initio DFT molecular dynamics

- Electrons are treated quantum mechanically, nuclei are treated as classical particles
- Electronic degree of freedom is treated within the Density Functional Theory under adiabatic approximation
  - PBE type Generalized Gradient Approximation is used to describe the electron-electron many-body exchange-correlation effect
- Time evolution of electrons and nuclei are calculated based on Car-Parrinello algorithm
- Lack of quantum effect is compensated by the use of higher temperature (400K)
  - Quantum zero-point motion energies of symmetric/anti-symmetric stretching, bending mode of $H_2O$ are much higher than ambient temperature (300K), which necessitates this treatment

# Technical backup slide 2: constructing the interface model

1. Using the **local bond topology models established by FY12,** construct realistic surface structure models
2. The interface model is made of repeated slabs of water and semiconductor in a periodic simulation box where the surface structure is taken from above
3. Molecular Dynamics simulations are performed with the Car-Parrinello algorithm at a constant temperature using the fictitious external heat bath

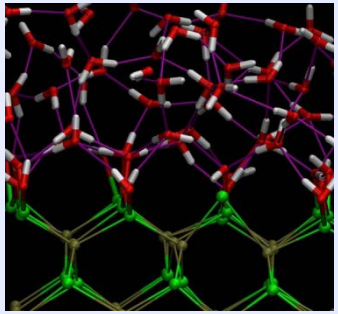
*Quantum-Espresso* code

DFT calculations

- periodic slab models
- PBE-GGA XC functional
- (2 x 4), (2 x 1), (1 x 2) reconstructions

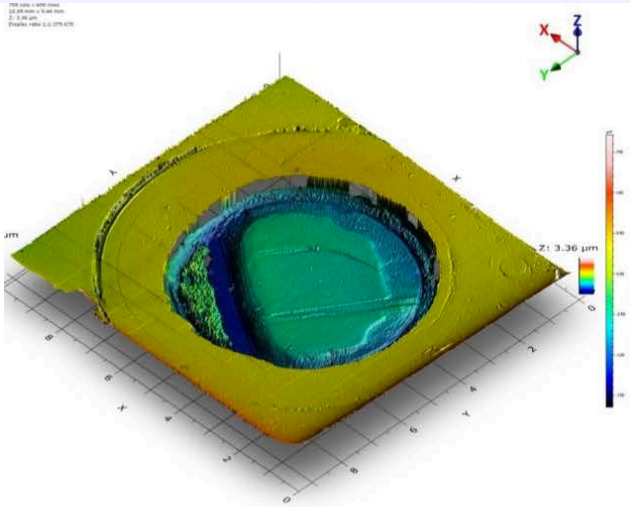
Car-Parrinello dynamics

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



# Technical backup slide 3: estimation of corrosion current by H. Wang (NREL)

After 24h,
*ca*. 0.52 ppm Ga found in 100 mL solution (ICP)




$$Ga = Ga^{3+} + 3e^-$$

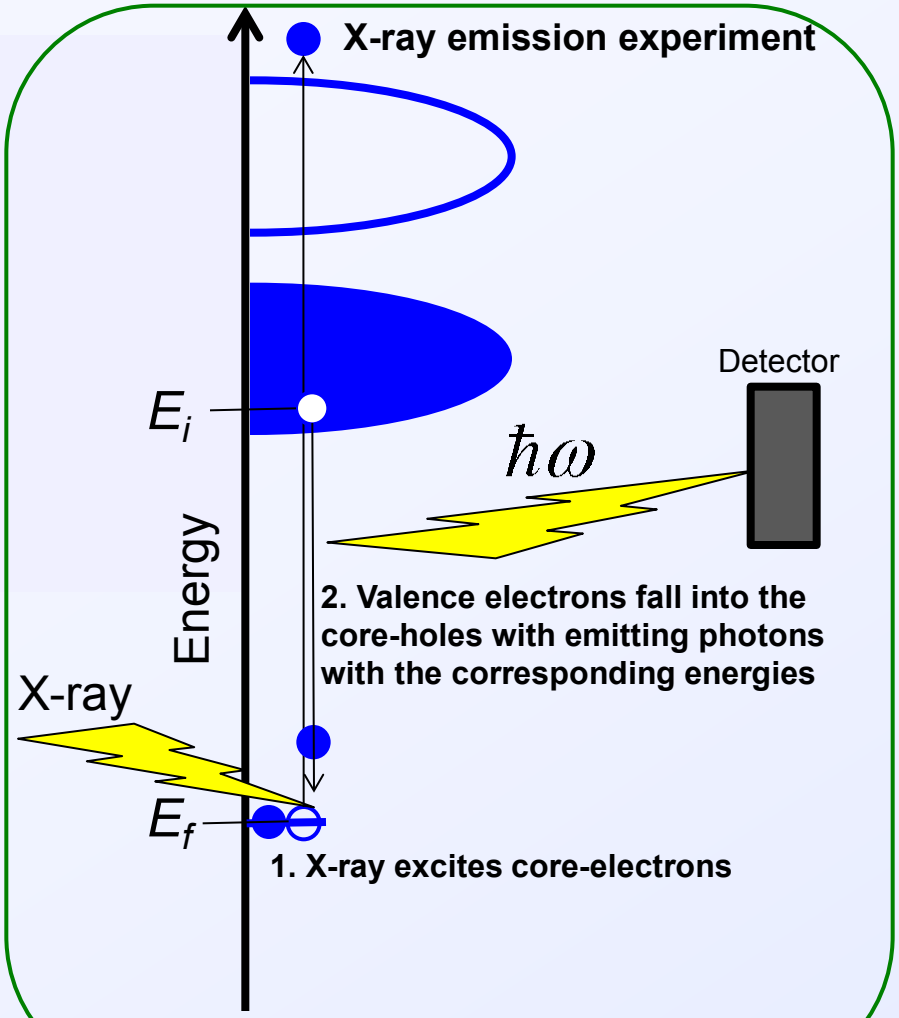
Take:
The 0.52 ppm Ga3+ found 100ml solution (ICP), Atomic weight of Ga = 69.7

➔ $0.52\times10^{-3}$(g/L)×0.1(L)/69.7(g)=$7.461\times10^{-7}$ mol

Equivalent to the charge: $7.461\times10^{-7}$ (mol)×3×96500 (C/mol) = 0.216 C

➔ Transfer to corrosion current:
0.216 (C)/[(24×3600)(s)×0.264($cm^2$)] = $9.47\times10^{-6}$ A/$cm^2$

# Technical backup 4: X-ray emission spectrum




Performed by UNLV at ALS

## X-ray emission spectrum calculations

$$\sigma(E) \propto \hbar\omega \left| \langle \psi_i | \vec{\varepsilon} \cdot \vec{r} | \psi_f \rangle \right|^2 \delta(E_f - E_i - \hbar\omega)$$

Polarization vector of X-ray (take average over x, y, z components in our case)

Initial/final states wavefunctions are calculated with DFT

Issues solved using reference systems (GaN/InN):

- Detector/disorder broadening (Gaussian)
- Lifetime broadening (Lorentzian)

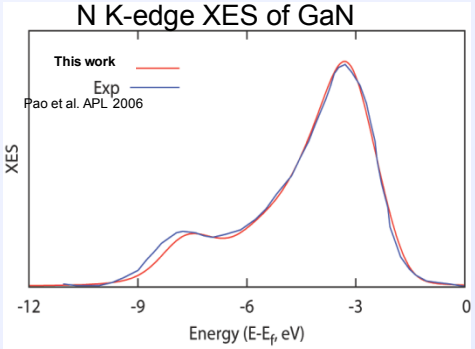
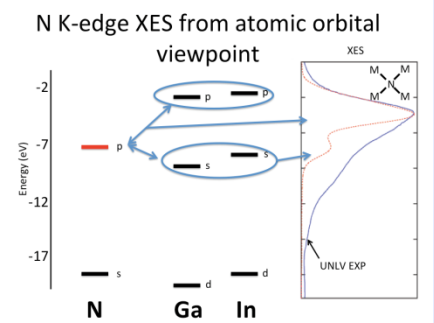
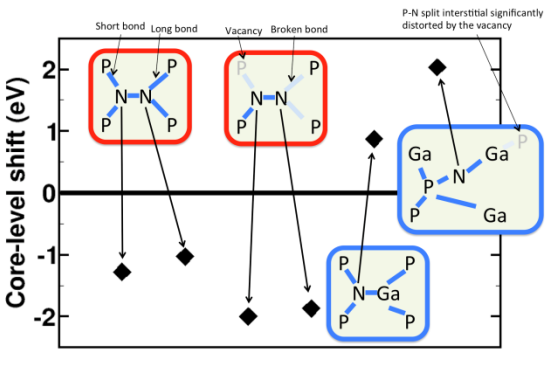
Issues addressed by rational thinking:

- How do we find the candidate N environment?
  - Atomic orbitals/hybridization/tendency of CLS (next slide)

WIP:

- Accurate calibration of energy scale to correct DFT error
  - UNLV will provide carefully measured data on GaN and on InN, and LLNL results will be calibrated to these data

LLNL/LBNL

# Technical backup slide 5: technical issues solved so far

- Broadening parameters are determined by fitting to published experimental data
  - Small scatter in N K-edge XES of InN found among of published results, therefore, additional experiments performed by UNLV (WIP)
- Rationally identifying appropriate candidate N environments using the following criteria
  - Both valence band and core-level shift contribute to XES
  - Relevant feature of balance band can be deduced from the knowledge on how atomic orbitals will hybridize, on the type of neighbor atoms, and on the coordination (where should the peak appear?)
  - Direction of core-level shift could be deduced from the type of surrounding atoms (anti-site/iso-electronic substitution: these shift the spectrum in opposite directions)
  - The spectral features are broadened by introduction of nearby vacancy (when the XES is too structured compared to experiments)