# II.C.4 Characterization and Optimization of Photoelectrode Surfaces for Solar-to-Chemical Fuel Conversion

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Project End Date: Project continuation and direction determined annually by DOE

## Overall Objectives

- Develop theoretical tool chest for modeling photoelectrochemical (PEC) materials to be used for synergistic theory, characterization, and synthesis activities.
- Uncover underlying mechanisms of surface corrosion and hydrogen evolution at the water-photoelectrode interface.
- Elucidate relationship between stability and efficiency.
- Use derived structure-property relationships to develop device improvement strategies.

## Fiscal Year (FY) 2013 Objectives

- Complete the *ab initio* simulations of water-InP and water-GaP interfaces, including data analysis and publication in peer-reviewed journals.
- Investigate corrosion mechanisms for III-V semiconductor electrodes.
- Identify chemical environments of $N_2^+$ bombardment-induced nitrogen impurities in $GaInP_2$, based on measured and calculated X-ray emission spectroscopy (XES) spectra.
- Publish results on simplified interfacial charge-transfer model for high-throughput assessment of PEC surface catalytic activity.
- Compile knowledge database of existing research on PEC electrode materials and interfaces, with emphasis on III-Vs and chalcogenides.

## Technical Barriers

This project addresses the following technical barriers from the Hydrogen Production section (3.1) of the Fuel Cell Technologies Office Multi-Year Research, Development, and Demonstration Plan [1]:

(AE) Materials Efficiency – Bulk and Interface

(AF) Materials Durability – Bulk and Interface

## Technical Targets

This project is conducting fundamental theoretical studies of mechanisms of corrosion and catalysis in semiconductor-based photoelectrode materials for PEC hydrogen production. Insights gained from these studies will be applied toward the optimization and design of semiconductor materials that meet the following DOE 2015 PEC hydrogen production targets (Table 3.1.8A in [1]):

- Solar-to-hydrogen (STH) energy conversion ratio: 15%
- Electrode replacement lifetime: 0.5 year

## FY 2013 Accomplishments

- Continued with compilation, review, and sharing of available information on III-V electrode materials, catalysts, and related subjects (ongoing).
- Began gathering available information on copper indium gallium diselenide electrodes as a lower-cost alternative to high-STH III-V semiconductors.
- Completed quantum molecular dynamics of water-electrode (GaP/InP) interfaces, and submitted two papers on the properties of interfacial water and wetted surfaces [2,3].
- Applied the simple model Hamiltonian approach developed in FY 2012 to an unconventional photoelectrode, $MoS_2$. A paper on this topic was submitted [4].
- The National Renewable Energy Laboratory (NREL) team conducted further experiments to validate the hole-trapping corrosion mechanism. This was one of three possible corrosion mechanisms identified in FY 2011 [5], for which supporting evidence emerged during group discussions in FY 2012 [6].
- Continued collaborations with unfunded external collaborators to develop theoretical tool chest for PEC hydrogen research.

- Continued joint theoretical/experimental XES study on III-V electrode surface (continue through FY 2013 and beyond).

## INTRODUCTION

Certain III-V-based PEC cells, notably the $GaInP_2$/GaAs tandem cell developed at NREL, are known to demonstrate high STH conversion efficiencies that are close to the DOE FY 2015 goal [1]. However, durability of these cells has remained the key unresolved issue so far. The primary purpose of this project is to perform a detailed investigation into the microscopic properties of the water-electrode interface, and to use this information to identify correlations with device performance, as measured in terms of STH conversion efficiency and corrosion resistance. The results will provide key feedback to collaborators at NREL, helping them develop a coherent performance optimization scheme for III-V-based photoelectrodes. State-of-art X-ray spectroscopic measurements performed by the University of Las Vegas (UNLV) team will bridge remaining gaps in the knowledge obtained from our atomistic modeling, facilitating comparison with actual electrode properties. In FY 2013, we had three major accomplishments [7]. First, our findings on the interfacial properties and their implications for the hydrogen evolution reaction (HER) and corrosion reactions were summarized in two papers submitted to peer-reviewed journals [2,3]. Second, the simple model Hamiltonian-based method tested in FY 2012 [6] was applied to $MoS_2$, and all results were summarized and submitted to a peer-reviewed journal [4]. Third, in order to determine the chemical environment of nitrogen impurities in $GaInP_2$ introduced by $N_2^+$ bombardment, a rational procedure to build model atomic structures that can reproduce the measured XES was developed, and the major nitrogen states were successfully identified [8].

## APPROACH

Further progress in semiconductor-based PEC photoelectrodes requires in-depth understanding of the complex relationship between surface stability and catalytic activity. This in turn relies on knowledge of the fundamental nature of the electrode-water interface, and of the chemical pathways explored during surface-active hydrogen evolution. As such, we are carrying out finite-temperature *ab initio* molecular dynamics simulations and energetics calculations based on density-functional theory to understand the chemical, structural, and electronic properties of water/electrode interfaces under equilibrium conditions, as well as to understand the competing chemical reaction pathways visited during photocatalysis. Our approach uses (001) surfaces of InP, GaP and $GaInP_2$ as model semiconductor electrodes. We are investigating on effect of the foreign chemical species on the stability and reactivity of the electrode surfaces, as suggested by our collaborators in J. Turner and T. Deutsch's group at NREL [9], as well as independent reports in the literature that surface oxygen may play a key role in motivating both the surface photocorrosion and the catalytic water splitting reaction [10,11]. Accordingly, we are evaluating the stability, structure and reactivity of the III-V(001)/water interfaces in the presence of surface oxygen, hydroxyl, and nitrogen, in order to correlate the results to experimentally observed surface compositions and morphologies. We also provide *ab initio* derived X-ray spectroscopic data to enable direct comparison with experimental results from Prof. C. Heske's group at UNLV. This information is intended to suggest a strategy for device improvement.

## RESULTS

About 1,200 papers related to PEC hydrogen research have been collected, indexed, and stored. Those deemed especially relevant to III-V semiconductor-based approaches have been summarized and shared with members of the III-V Surface Validation Team (LLNL/NREL/UNLV) of the DOE Photoelectrochemical Hydrogen Production Working Group using a limited-access community web forum and traditional email communication. Particular emphasis was put on $GaInP_2$, $In_2O_3$, the growth interface between the two, co-catalyst, and corrosion mechanisms, since these are expected to be crucial for identifying the agent responsible for corrosion resistance and hydrogen evolution.

Detailed studies of InP and GaP (001) surfaces and their interfaces with water were summarized as two separate papers and submitted to peer reviewed journals [2,3]. As a continuation of previous studies on these surfaces and the effect of oxidation and/or hydroxylation [12], the first paper discussed how these surfaces are affected by contact with bulk water [3]. We previously showed that oxidized surfaces facilitate water dissociation, which leads to surface hydroxylation [12]. A consistent behavior was observed during *ab initio* molecular dynamics of water/III-V interfaces, where the formation of an ice-like hydrogen-bond network was observed near both InP and GaP. No major significant differences were observed in the structural and electronic properties of the two surfaces [3]. In contrast, the properties of interfacial water near GaP(001) and InP(001) were found to exhibit a peculiar difference [2]. In particular, at the GaP (001)-water interface, a clear gap in the hydrogen-bond network was found between the surface adsorbants (O, OH, or $H_2O$) and bulk water, while at the InP (001)-water interface, the hydrogen-bond network is continuous and dynamic. Further analysis suggested that these differences will lead to differences in surface proton transport properties at these interfaces: it is facile at the InP-water interface, while likely to be hindered at the GaP-water

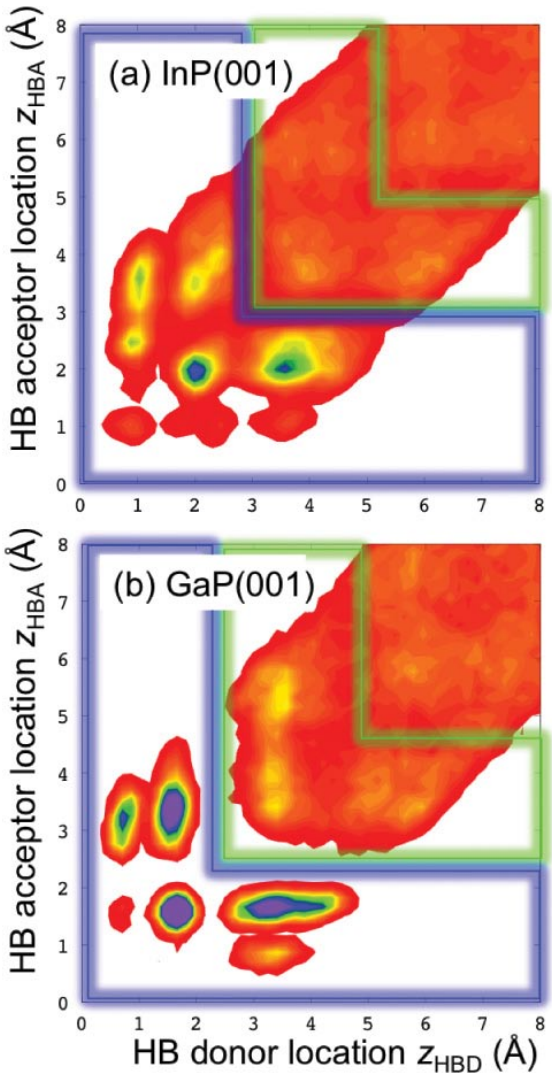


**FIGURE 1.** Probability density of locations (measured perpendicular to the surface) of hydrogen-bond donor-acceptor pairs in water at the interface with (a) InP(001) and (b) GaP(001). The simulations account for native surface hydroxylation [2].

interface. Possible scenarios for the relationship between the proton transport property and photoelectrode performance/corrosion resistance are discussed in detail [2]. These include differences in HER and corrosion mechanisms, as well as the influence of surface catalysts on these mechanisms.

During a Working Group teleconference held in FY 2012, we proposed a "dark" current experiment, in which electrons are provided by a power source to the cathode rather than by photoillumination. This allows one to identify whether cathodic hole transport, which is relevant only in the case of photoillumination where electrons and holes are co-generated, plays a role in the corrosion mechanism. If hole trapping is the major source of corrosion, the rate of corrosion should be greatly suppressed in a dark current experiment. In addition to the published results [13] found during the FY 2012 discussion [6], more experiments were conducted by NREL in FY 2013. It was shown that the rate of corrosion is linear to the photoillumination (i.e., hole concentration) [7]. This supports our assertion that the hole-trapping corrosion mechanism is the major contributor for III-V-based photocathode. Further investigation is desired to understand the nature of hole-traps in order to develop an effective mitigation strategy.

Motivated by the reported stability of GaN as a photoelectrode [14,15], the effect of nitrogen bombardment on the $GaInP_2$ surfaces has been being studied by NREL during FY 2012 [16] and FY 2013 [17]. The spectroscopy team at UNLV performed a series of measurements including N K-edge XES on these nitrogen-treated electrodes [18]. Our earlier XES simulations results indicated that the chemical environments of nitrogen impurities were not pure substitutional impurities. In FY 2013, we have developed a rational scheme to determine the relevant chemical environment of nitrogen based on a consideration of the following factors [7]: (1) expected shape and positions of XES peaks based on the atomic levels and their hybridization; (2) chemical shifts from the environment; and (3) spectral broadening due to vacancy-induced structural distortions. Our results indicated that a significant number of nitrogen impurities are forming various types of vacancy-interstitial complexes, suggesting that more thermodynamically driven approach might be suitable in forming a thin layer of less defective nitride compound (assuming that defects would have negative impact on STH efficiency and/or corrosion resistance). We point out that the developed procedure described above is generally applicable to an arbitrary system and currently being summarized in order to publish in a peer reviewed journal [8].

Finally, the model Hamiltonian approach developed by Santos et al. [19] tested in FY 2012 [6] was applied to the protonation process on a $MoS_2$ electrode. This method is based on Markus-Hush theory and the Anderson-Newns model, and is able to simultaneously address $H^+$ solvation, charge transfer reactions, and chemisorption very simply and with relatively low computational cost. This approach was tested with Pt in the original work [19] and with $GaInP_2$ in FY 2012 [6], where it was confirmed that the model is able to reproduce qualitatively correct behavior of protonation on these systems under a bias potential. On Pt, proton adsorption and reduction is exothermic and barrier-free, while on $GaInP_2$, it is exothermic with a large barrier. Our new results on $MoS_2$ showed that protonation on the Mo site has a negligibly small energy barrier with favorable binding energy for the HER. This was attributed to an appropriate strength of interaction between relevant orbitals of H and Mo (see Figure 3). The S site might have a reasonable protonation free energy profile if the surrounding atoms were able to relax fast enough compared to the time scale of protonation (quasi-adiabatic). We also found that the proton binding energy could be modulated by solvation, due to

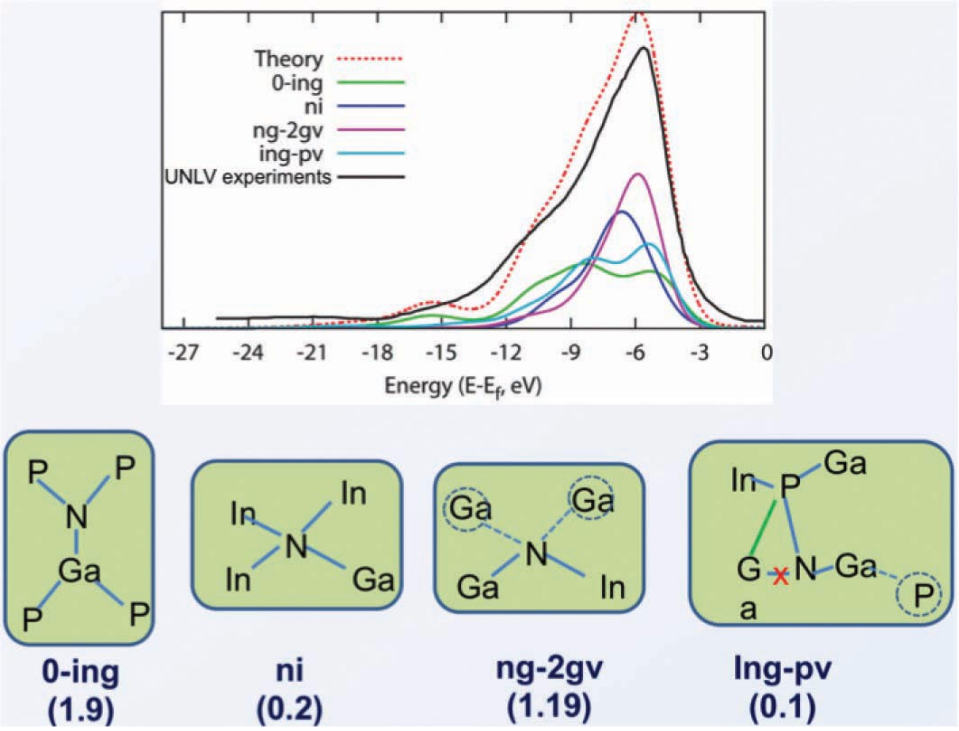


**FIGURE 2.** Calculated XES spectra corresponding to different possible nitrogen environments in nitridated $GaInP_2$, shown schematically below the graph. The total calculated spectrum (red dotted) is a fit to the experimental spectrum (black) based on a weighted sum of these calculated components [8].

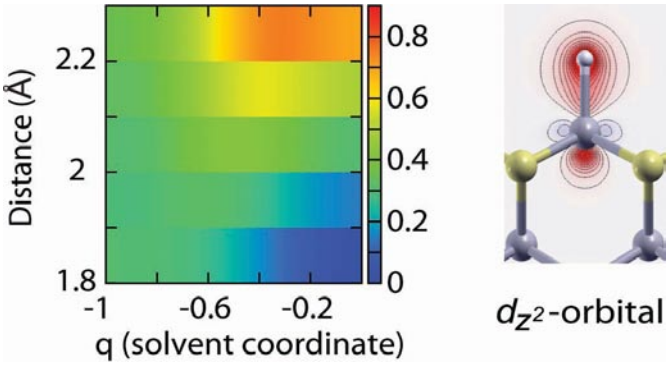


**FIGURE 3.** Left: calculated free energy profile for the protonation at the Mo site on $MoS_2$ as functions of solvent coordinate and Mo-H distance [4]. Right: the Mo-H bonding orbital that contributes to the low barrier protonation where the $dz^2$ character is clearly seen [4].

sizable polarization. All of these results were summarized and submitted to a peer-reviewed journal [4]. We emphasize that this approach provides a high-throughput way to gain insights on the underlying mechanisms that responsible for favorable/unfavorable free energy profile of protonation in different materials, which could be very useful for designing a novel catalytic material.

## CONCLUSIONS AND FUTURE DIRECTIONS

- The studies of water/III-V interface performed during FY 2010-FY 2013 were summarized as two papers and submitted to peer-reviewed journals.
- The study of the catalytic reaction process on $MoS_2$ based on the *ab initio*-derived simple model Hamiltonian were summarized and submitted to a peer-reviewed journal.
- The linear relation between the hole-carrier concentration and the rate of corrosion was shown by the experiments conducted by NREL in FY 2013. Discussions for developing a research plan for understanding the precise nature of hole-traps responsible for the observed corrosion underway.
- Using theoretical and experimental N K-edge XES spectra, the procedure to construct model atomic structures of impurities in semiconductor electrode was established. Based on this, we have identified the major chemical states of nitrogen impurities that were introduced to $GaInP_2$ by $N_2^+$ bombardment.
- The compilation of past studies will continue in order to refine our growing understanding of the relevant issues of photoelectrochemistry, particularly with respect to III-V surfaces, their oxides, and interfaces between them.

This effort will be expanded to the other materials and catalysts in FY 2014.

- Develop deeper understanding on the role of thermodynamics and kinetics in HER and in corrosion for a given photoelectrode material in order to identify an effective corrosion mitigation strategy.

## FY 2013 PUBLICATIONS/PRESENTATIONS

### Publications

**1.** T. Ogitsu, B. Wood, W. Choi, *DOE Fuel Cell Technology Hydrogen Program Annual Merit Review* (2013).

**2.** B.C. Wood, E. Schwegler, W.-Ih Choi, and T. Ogitsu, "Aspects of the surface chemistry of GaP(001) and InP(001) in contact with water," submitted.

**3.** B.C. Wood, E. Schwegler, W.-Ih Choi, and T. Ogitsu, "Hydrogen-bond dynamics of water at the interface with InP/GaP(001) and its implications for photoelectrochemistry," submitted.

**4.** W.-I. Choi, B. Wood, E. Schwegler, and T. Ogitsu, "Site-dependent free energy barrier for proton reduction on $MoS_2$ edges," submitted.

**5.** W.-I. Choi, M. Weir, T. Deutsch, T. Williamson, L. Weinhardt, A. Benkert, M. Blum, F. Meyer, M. Bär, K. George, B.C. Wood, D. Prendergast, E. Schwegler, J. Turner, C. Heske, and T. Ogitsu, "Chemical environments of implanted nitrogen in $GaInP_2$ characterized with X-ray emission spectroscopy," in preparation.

### Presentations

**1.** PRiME 2012, Honolulu, HI, Oct 2012 (invited).

**2.** Physics Colloquium at UT Arlington, Arlington, TX, Oct 2012 (invited seminar).

**3.** Invited seminar at U. South Florida, Jan 2013.

**4.** WIP progress report presentation at DOE PEC hydrogen WF meeting at UNLV, Jan 2013.

**5.** American Physical Society March Meeting in Baltimore, March 2013 (two presentations).

**6.** 2013 Materials Research Society Spring Meeting in San Francisco, April 2013.

**7.** 223rd ECS Meeting in Toronto, May 2013 (invited).

**8.** DOE EERE Fuel Cell Technology Annual Merit Review in Arlington, May 2013.

**9.** Invited seminar at Sandia National Laboratory, July 2013.

**10.** SPIE conference, San Diego, August 2013 (invited).

**11.** CPMD-Meeting 2013, Matter, life, light from ab initio molecular dynamics simulations, Leipzig, September 2013 (invited).

**12.** American Chemical Society Fall Meeting, Indianapolis, September 2013 (invited).

**13.** JSAP-MRS Joint Symposia, Kyoto, September 2013 (oral).

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**3.** B. Wood, E. Schwegler, W.-Ih Choi, and T. Ogitsu, "Aspects of the surface chemistry of GaP(001) and InP(001) in contact with water," submitted.

**4.** W.-Ih Choi, B. Wood, E. Schwegler, T. Ogitsu, "Site-dependent free energy barrier for proton reduction on $MoS_2$ edges," submitted.

**5.** T. Ogitsu, B. Wood, W. Choi, *DOE Fuel Cell Technology Hydrogen Program Annual Merit Review* (2011).

**6.** T. Ogitsu, B. Wood, W. Choi, *DOE Fuel Cell Technology Hydrogen Program Annual Merit Review* (2012).

**7.** T. Ogitsu, B. Wood, W. Choi, *DOE Fuel Cell Technology Hydrogen Program Annual Merit Review* (2013).

**8.** W.-I. Choi, M. Weir, T. Deutsch, T. Williamson, L. Weinhardt, A. Benkert, M. Blum, F. Meyer, M. Bär, K. George, B.C. Wood, D. Prendergast, E. Schwegler, J. Turner, C. Heske, and T. Ogitsu, "Chemical environments of implanted nitrogen in $GaInP_2$ characterized with X-ray emission spectroscopy," in preparation.

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**18.** C. Heske *et al.*, *DOE Fuel Cell Technology Hydrogen Program Annual Merit Review* (2012).

**19.** E. Santos *et al.*, *Phys. Rev. B* **79**, 235436 (2009).