

II.G.3 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

Fiscal Year (FY) 2011 Objectives

- Develop theoretical tool chest for modeling photoelectrochemical (PEC) systems, including experimental validation using model III-V 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 the University of Nevada, Las Vegas (UNLV) for interpretation of experimental results and validation of theoretical models.
- Share research insights with the PEC Working Group members

Technical Barriers

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

- (Z) Materials Durability
- (Y) Materials Efficiency

Technical Targets

This project is conducting fundamental theoretical studies of mechanisms of corrosion and catalysis in III-V

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 2013 PEC hydrogen production targets:

- Usable semiconductor bandgap: 1.8-2.3 eV
- Chemical conversion process efficiency: 10%
- Plant solar-to-hydrogen efficiency: 8%
- Plant durability: 1,000 hrs.

FY 2011 Accomplishments

- Compiled, reviewed, and shared available information on III-V electrode materials (ongoing).
- Performed quantum molecular dynamics of water-electrode interfaces:
 - Evaluated importance of surface oxygen in determining reactivity. In FY 2010, we discovered that bonding topology of oxygen at InP(001) surface dictates the catalytic activity for water splitting. In FY 2011, we expanded this study to include different III-V (GaP), and on wider variety of surface morphology. Quantitative reaction energetics were provided.
 - Established validity of local topological model and used it to extract model surfaces for further study (FY 2011).
- Group discussion of results led to formulation of three possible corrosion mechanisms (FY 2011).
- Recruited four external collaborators to develop theory/computational tool chest for PEC hydrogen research.
- Began joint theoretical/experimental study on III-V electrode surface (continue through FY11).



Introduction

Development of efficient processes for the carbon-free production of hydrogen is key to sustainable realization of a future hydrogen economy. One particularly promising approach is to use sunlight to catalyze direct evolution of hydrogen from water in a PEC cell. Semiconductor-based PEC devices are particularly attractive, thanks to a relatively simple device design and a wealth of data available for engineering efficient photon harvesting [1]. Results have demonstrated that one can achieve solar-to-fuel conversion efficiency in excess of the 2013 DOE targets (>12% using a tandem GaAs/GaInP₂ cell); however, this has come at the expense of short device lifetime due to fast degradation

of the electrode [2]. Further progress has been hindered by a poor understanding of the fundamental chemical processes operating at the electrode-water interface. Our research addresses this need from a theoretical perspective, leveraging realistic *ab-initio* simulations to determine the key mechanisms governing corrosion and catalysis at the water-semiconductor interface.

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 GaInP₂, which have known water-splitting activity, 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's group at the National Renewable Energy Laboratory (NREL) [3] and reports in the literature that surface oxygen may play a key role in motivating both the surface photocorrosion and the catalytic water splitting reaction [4,5]. 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. Heske's group at UNLV. This information is intended to suggest a strategy for device improvement.

Results

Over 700 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. Particularly detailed reviews were completed on GaInP₂, In₂O₃, and the growth interface between the two. We have discovered literature that points to competition between ordered and disordered surface phases, which can rationalize inconsistencies in device performance observed in NREL experiments. We have also reviewed literature suggesting the relevance of surface oxide growth for realizing both device performance

and corrosion resistance. However, we also found reports that thin native oxide formation on III-V semiconductors can give rise to undesirable electrical properties if the oxide/III-V interface is rough [6]. Based on this review, it was suggested that careful, controlled growth of a high quality oxide layer on III-V semiconductor might improve the durability without compromising the hydrogen production efficiency.

In FY 2010, we studied (meta)stable surface structures of oxide and hydroxide on InP(001). We found that there are two categories of oxygen bonding configurations, In-O-In and In-O-P, consistent with experimental observations [7]. We then studied the reactivity of a water molecule on these surfaces and found that spontaneous dissociative adsorption is observed only at the In-O-In site. In FY 2011, we significantly expanded this study in order to have a more complete understanding, accounting for a wider variety of possible surface structures and looking at other III-V semiconductors, including GaP. Despite minor differences, we were able to definitively conclude that the strong correlation between the chemical activity and the local bonding topology is universal, and that III-O-III is chemically active against H₂O adsorption, while III-O-V is not (Figures 1 and 2).

When immersed in electrolyte, the electrode surface adopts a very complex morphology containing combinations of surface oxide and hydroxide. As such, efficient computational modeling using *ab-initio* techniques becomes very challenging due to exponential growth of the number of possible configurations. To address this issue, we have employed the Cluster Expansion method [8], in which the surface adsorption energetics is modeled by an Ising-type Hamiltonian, with interaction parameters fitted to total energies obtained using density functional theory. Using this method, we calculated the total energies of hydroxylated InP(001) surface as a function of OH coverage. We found that the ground-state energy varies little over a wide range of OH coverage, meaning varying concentrations of surface OH can be expected under realistic operating conditions (Figure 3). In contrast, the oxidized surface carries significant coverage dependence.

In addition, several *ab-initio* molecular dynamics simulations of III-V/water interfaces have been performed during FY 2010/FY 2011. These have led to the following findings: (1) On oxidized or hydroxylated cation (III group)-rich (001) surfaces, the hydrogen bonding network formed by the electrolyte in contact with surface O or OH is strengthened and becomes considerably less dynamic compared to the same network in bulk water; (2) Water molecules nearby oxygen atoms in a In-O-In bonding configuration show a high probability of dissociative adsorption, whereas the reactivity is negligible near oxygen sites in a In-O-P bonding topology, confirming our previous findings; and (3) Dissociative adsorption of H₂O is accompanied by collective motion of surrounding water molecules, which acquire enhanced hydrogen-bond strength.

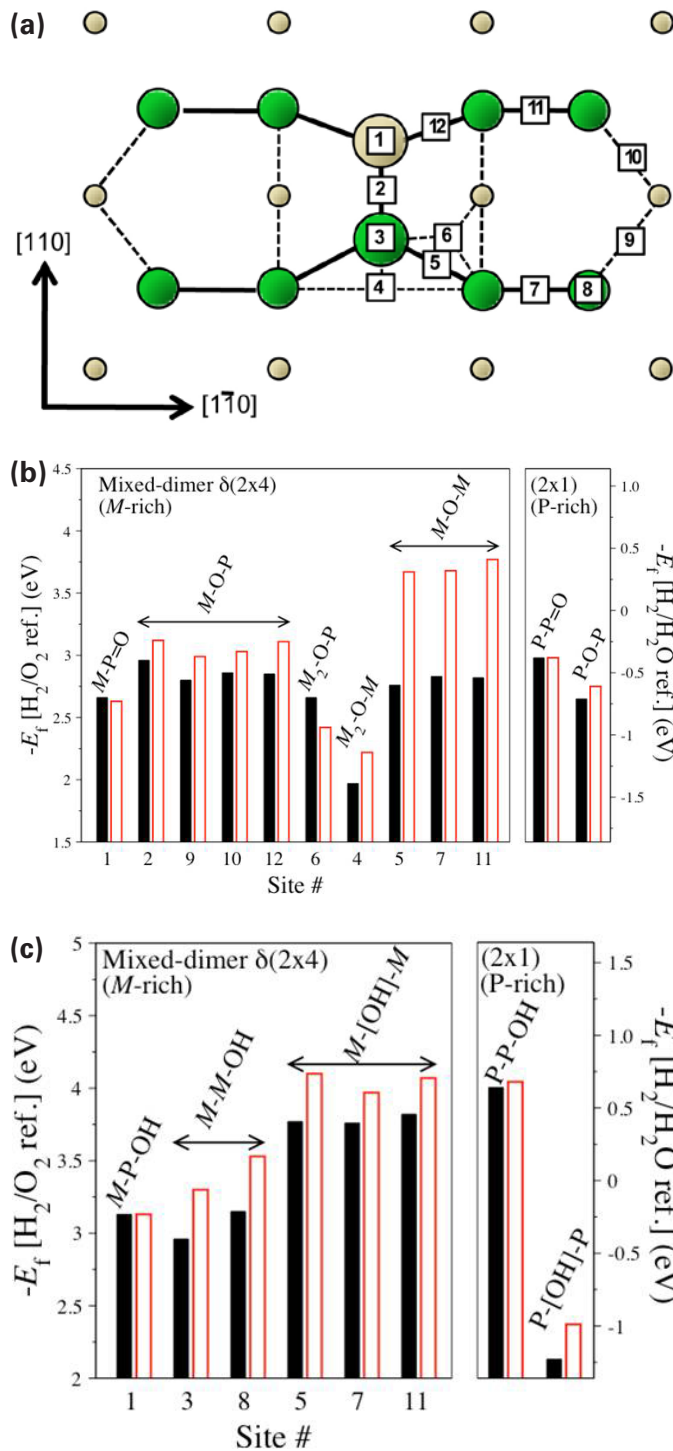


FIGURE 1. Oxygen and hydroxyl adsorption energies on δ -(4x2) type InP and GaP (001) surfaces. (a) Schematic diagram of δ -(4x2) reconstructed surface. Green spheres correspond to cation atoms (In or Ga), and grey spheres correspond to phosphorus atoms. (b) Oxygen adsorption energies and (c) hydroxyl adsorption energies for the sites defined in (a). In (b) and (c), filled bars are for InP and open bars are for GaP.

At the III-V Surface Validation Team meetings and teleconferences, we have discussed three possible corrosion

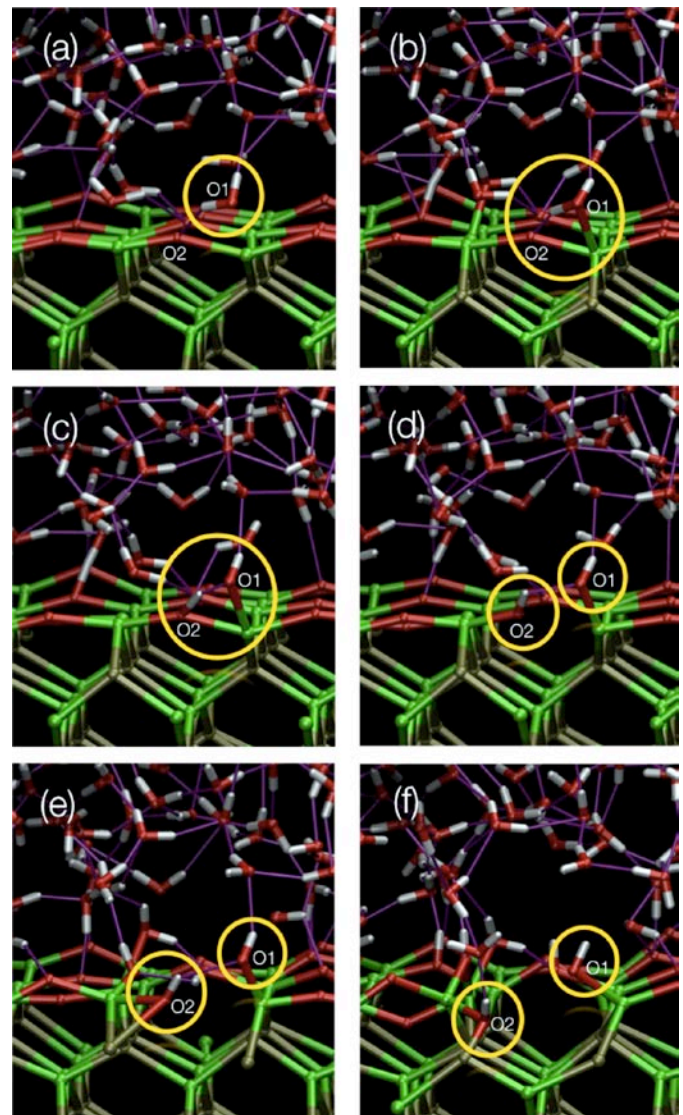


FIGURE 2. Snapshots of dissociative adsorption of a water molecule observed during our *ab-initio* dynamics simulation of the water-InP(001) interface. The yellow circles highlight the water molecule of interest (O1) and the oxygen atom that induces the dissociative adsorption (O2). (a) The water molecule (O1) is pulled toward an oxygen bound to two In atoms (O2). (b) O1 is bound to an In atom, with a hydrogen bond between its attached proton and O2. (c) The proton is transferred from O1 to O2. (d) One of the In-O bonds of O2 is broken. (e), (f) Two OH species are formed.

mechanisms based on combined results from our theoretical study, available information in literature, and experiments performed by other members of the Team. (1) The presence of hole-trap states introduced by defects and impurities are a known cause of semiconductor device degradation. We found two possible scenarios that could contribute to hole trapping in our III-V models: first, formation of specific atomic configurations that lead to the spatially and energetically localized surface states near the Fermi level, which we found could be induced either by chemically or mechanically; and second, an accumulation of anions at

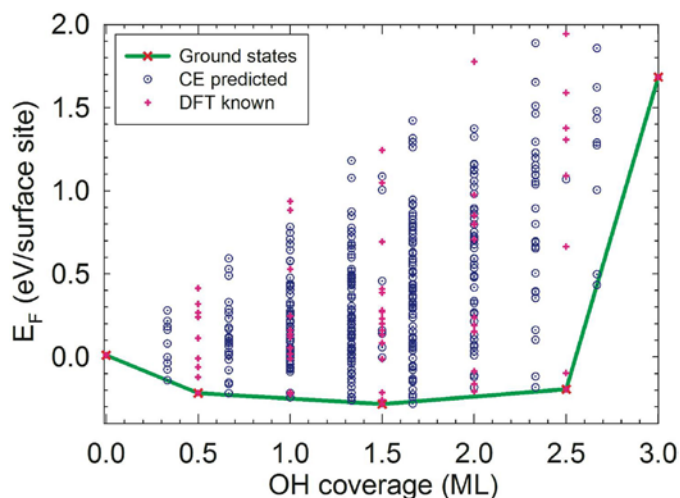


FIGURE 3. The OH adsorption energies as a function of OH concentration calculated by the Cluster Expansion (CE) method and Density Functional Theory (DFT).

the oxide/III-V interface, which is known to take place during natural oxide growth of III-V semiconductors [7]. (2) The formation of locally anodic regions can cause dissolution within the cathode due to loss of cathodic protection from a short-circuit current. Such regions can be formed by intrinsic inhomogeneity in the composition of the cathode material itself, or else by concentration gradients of adsorbed chemical species, such as OH. The former could be particularly relevant for GaInP₂ since this material is known to exhibit incomplete ordering, with ordered and disordered regions displaying distinct electronic properties (e.g., different bandgaps). (3) Undercoordinated cation atoms, which are often observed in our *ab-initio* molecular dynamics simulations as a consequence of local finite-temperature fluctuations in surface composition, can facilitate rapid direct dissolution of surface metal atoms.

In order to formulate an effective corrosion mitigation strategy, it is necessary to assess the likelihood of each of the aforementioned proposed corrosion mechanisms with appropriate experimental methods. Accordingly, the III-V Surface Validation Team plans to perform in situ X-ray spectroscopy studies of the photoelectrode-electrolyte system under illumination. Our contribution to this effort will be provide *ab-initio* derived theoretical spectra for interpretation of experimental results. In preparation, we have performed an initial assessment on accuracy of theoretical X-ray emission spectra using three reference bulk systems: InP, GaP and GaInP₂. We have confirmed that the calculated spectra show satisfactory agreement with the experimental data obtained by our III-V Surface Validation Team collaborators at UNLV, (Figure 4).

In order to develop a complete theoretical/computational tool chest for PEC hydrogen production research, we have established collaborations with the

following four external researchers with specialized expertise: (1) Dr. David Prendergast at The Molecular Foundry (TMF), LBNL—First-principles X-ray Absorption/Emission Spectrum calculations of water-electrode interfaces (with whom we have a peer-reviewed TMF user project); (2) Prof. Chris Wolverton, Northwestern University—Cluster Expansion [8] for realistic modeling of III-V surfaces; (3) Dr. Minoru Otani, National Institute of Advanced Industrial Science and Technology, Japan—First-principles Effective Screening Medium method [9] to simulate interfaces under a bias voltage (part of the Japan-U.S. Ministry of Economy, Trade and Industry-DOE Clean Energy Technology Action Plan [10]). (4) Dr. Yoshitaka Tateyama, National Institute for Materials Science, Japan—First-principles methodology for simulation of redox potentials for charge transfer reactions at liquid/solid interfaces [11]. All collaborators have external research funding and do not require any additional cost to DOE.

Conclusions and Future Directions

- We have conducted extensive first-principles studies on native oxide formation on III-V (001) surfaces (III: In, Ga; V: P), and identified similarities and differences in the local bonding arrangement around the oxygen atom.
- Gas-phase water molecule adsorption simulations as well as *ab-initio* molecular dynamics simulations of water/III-V interfaces consistently show that III-O-III type local bonding arrangement induces dissociative adsorption of bound water, while III-O-V does not.
- We will investigate the link between the local chemical activity and the known macroscopic chemical behaviors, namely, corrosion and hydrogen evolution. The key technique will be to compare simulated spectral data to experiments by UNLV/NREL, with the specific goal of validating our proposed corrosion mechanisms. We will also work to ascertain the effect of surface nitridation on the relevant chemical reactions, motivated by its proven corrosion protection in recent experimental studies by NREL.
- We will design additional theoretical studies to refine our models of interfacial charge transfer reactions, leveraging the expertise of our separately-funded external collaborators. This will focus on the impact of photo-illumination, since the studies conducted to date considered only the properties of the interface precursory to illumination.

Special Recognitions & Awards

1. Best Poster Award, “Materials for Energy Applications: Experiment, Modeling, and Simulation” Conference, Los Angeles, CA, (2011).
2. Best Poster Award, LLNL Postdoctoral Poster Symposium (2010).

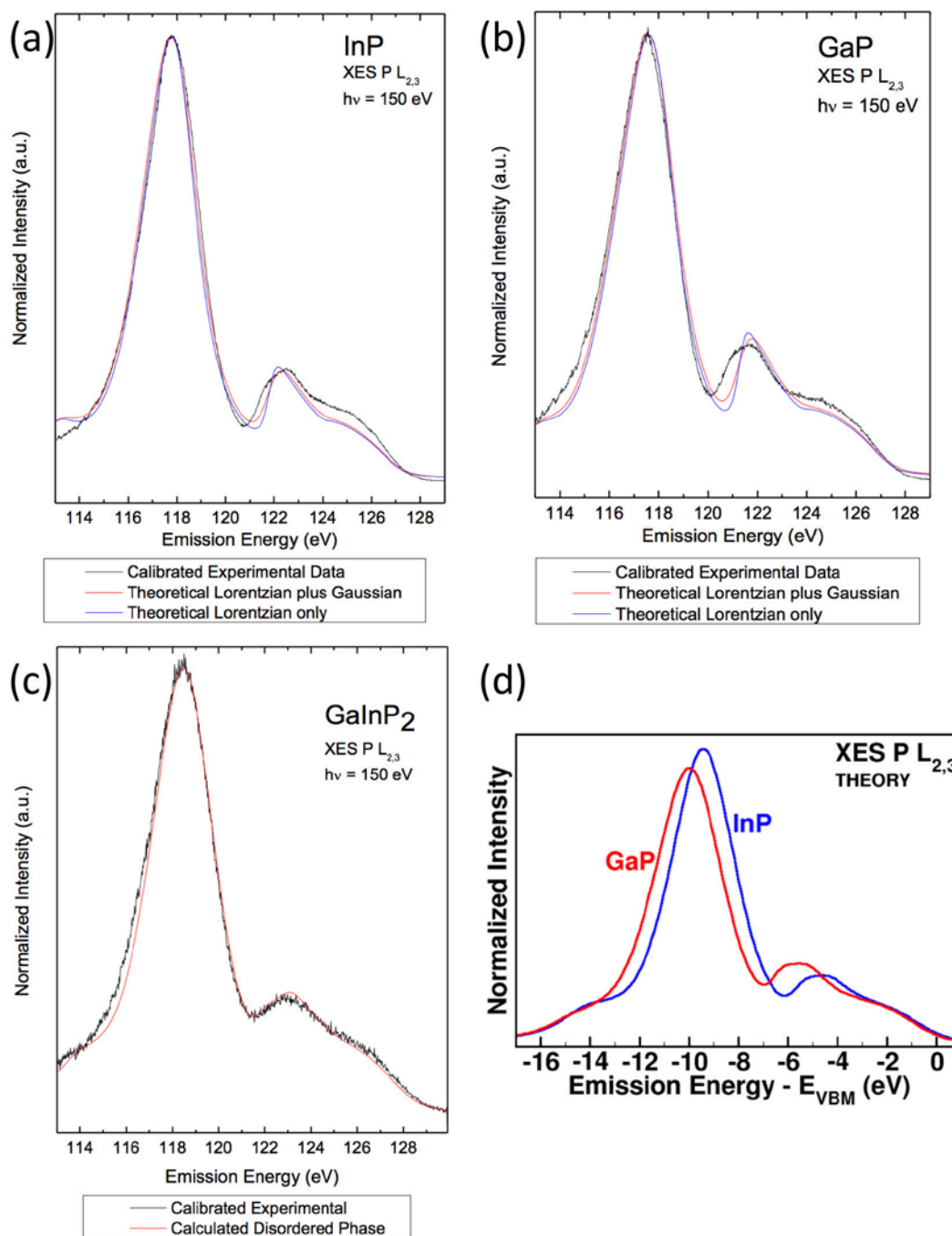


FIGURE 4. Calculated and measured phosphorus $L_{2,3}$ edge X-ray emission spectroscopy (XES) of bulk (a) InP, (b) GaP, and (c) GaInP₂. The experimental data is from Prof. Heske, UNLV. (d) The XES spectra of InP and GaP show clear differences. This indicates that a phase segregation of GaInP₂ into GaP and InP is detectable using XES measurements.

FY 2011 Publications/Presentations

Publications

1. B.C. Wood, T. Ogitsu, and E. Schwegler, "Ab-initio modeling of water-semiconductor interfaces for photocatalytic water splitting: The role of surface oxygen and hydroxyl," *Journal of Photonics for Energy* (in press).

2. B.C. Wood, T. Ogitsu, and E. Schwegler, "Ab-initio modeling of water-semiconductor interfaces for direct solar-to-chemical energy conversion," *Solar Hydrogen and Nanotechnology V, SPIE Proceedings 7770*, 77700E (2010).

3. B.C. Wood, T. Ogitsu, and E. Schwegler, "Characterization and optimization of photoelectrode surfaces for solar-to-chemical fuel conversion," *Proceedings of the 2011 DOE Hydrogen Program Annual Merit Review* (2011).

Presentations

1. “Progress in *ab-initio* modeling of III-V semiconductor-water interfaces for photoelectrochemical hydrogen production,” Hu’a Iki DOE Photoelectrochemical-IEA/HIA Joint Meeting, Honolulu, HI, December 2010.
2. “*Ab-initio* modeling of water-semiconductor interfaces for photoelectrochemical hydrogen production,” AIST, Japan, November 2010.
3. “A first-principles investigation of III-V semiconductor-water interfaces for solar hydrogen production,” 2011 Materials Research Society Spring Meeting, San Francisco, CA, April 2011.
4. “A first-principles investigation of III-V semiconductor-water interfaces for solar hydrogen production,” 2011 American Physical Society March Meeting, Dallas, TX, March 2011.
5. “Structure and reactivity of III-V semiconductors for photoelectrochemical hydrogen production,” 241st American Chemical Society National Meeting, Anaheim, CA, March 2011.
6. “Structure and reactivity of III-V electrode materials for photoelectrochemical H₂ production,” 2011 Materials for Energy Applications: Experiment, Modeling, and Simulations, Los Angeles, CA, April 2011.
7. “Characterization and optimization of photoelectrode surfaces for solar-to-chemical fuel conversion,” 2011 DOE Hydrogen Program Annual Merit Review, Washington, D.C., May 2011.

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