II.D.3 Characterization and Optimization of Photoelectrode Surfaces for Solar-to-Chemical Fuel Conversion

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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) 2014 Objectives

- Summarize the ab initio studies of water-InP and water-GaP interfaces, the development of ab initio-derived Model Hamiltonian for rapid screening of catalyst materials, and the interpretation of X-ray spectroscopic data relevant for corrosion mitigation mechanism, publish in peer-reviewed journals.

- Analyze the N/Ru/Pt based surface treatment experimental results provided by the National Renewable Energy Laboratory (NREL) and the University of Nevada, Las Vegas (UNLV) and develop a research and development plan for an effective corrosion mitigation method with the surface validation (SV) team members.

- Develop a theoretical hydrogen evolution reaction (HER) model, which takes hydrogen diffusion at the interface between III-V and electrolyte into account. The model

is to design an optimized co-catalyst arrangement for a cost-effective photoelectrode.

- Compile knowledge database of existing research on PEC electrode materials (ex. III-Vs and GIGS), interfaces and the other relevant subjects such as catalyst and X-ray spectroscopy.

Technical Barriers

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

(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 ref. [1]):

- Solar-to-Hydrogen (STH) Energy Conversion Ratio: 15%

- Electrode Replacement Lifetime: 0.5 year

FY 2014 Accomplishments

- Continued with compilation, review, and sharing of available information on III-V electrode materials, catalysts, and related subjects (ongoing).

- Three publications in peer reviewed journals.

- A novel hydrogen evolution reaction model, which takes hydrogen diffusion at the interface between III-V electrode and electrolyte into account, has been proposed.

  – The model might open up a new design strategy for improved STH conversion efficiency and optimal co-catalyst use (i.e. reduced cost).

- Continued collaborations with unfunded external collaborators to develop theoretical tool chest for PEC hydrogen research.

- Continued joint theoretical/experimental X-ray spectroscopy study on III-V electrode surface (continue through FY 2014 and beyond).

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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 UNLV team will bridge remaining gaps in the knowledge obtained from our atomistic modeling, facilitating comparison with actual electrode properties. In FY 2014, we had three major accomplishments. First, the results on III-V surface and interfaces as well as development of ab initio-derived Model Hamiltonian method for catalyst screening have been summarized and published as three papers in peer reviewed journals. Second, potential importance of interfacial H diffusion (publication 2) has led to development of a novel HER model, which could be used to investigate on a better surface treatment and co-catalyst arrangement. Third, as a part of the SV team, we have contributed in improved understanding of the relevant control parameter for $GaInP_2$ surface treatment based on nitrogen and Cu/Pt impurity.

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 the 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 [2], 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 [3,4]. 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 provided 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 1,750 papers relevant for PEC hydrogen research have been collected, indexed, and stored. Important information for the NREL/UNLV collaborators was summarized and shared using online tools such as email or photoelectrochemical.sharepointsite.net (Contact: Heli Wang of NREL). Comprehensive analysis on the acquired knowledge from literatures combined with detailed information on the experimental condition provided by NREL and with the UNLV spectroscopic information [7] led to identification of a few possible causes of performance variability: partial segregation of $GaInP_2$ into thin layers of InP and GaP [5, 6] and co-existence of ordered/disordered phases of $GaInP_2$ [8-12]. The former was primarily motivated by the results of photoemission spectroscopy and inverse photoemission spectroscopy measurements, where careful non-destructive surface cleaning using low energy ion sputtering was performed simultaneously. The $GaInP_2$ sample provided by NREL, after the cleaning, has shown that the surface band gap of about 1.3 eV [7], significantly smaller than known value of E_g ~1.8-2 eV [8-12] for $GaInP_2$. This value is rather close to that of InP. It is known that $GaInP_2$ is not thermodynamically stable against segregation into GaP and InP [5,6], therefore, it was conjectured that the photelectrode used by NREL might have the segregation problem, which might have contributed partly to the performance reproducibility issue. Also, it was discussed that the disordered phase has a higher conduction band edge position and the wider band gap [8-12], which is an advantage for the top absorber for tandem PEC cell, however, at the expense of shorter charger carrier lifetime [13]. There are many conflicting material behaviors, and therefore, it is very important to have comprehensive understanding of basic material properties in order to develop an effective research plan.

The research based on ab initio simulations of III-V surfaces and interfaces as well as on ab initio-derived model Hamiltonian for catalytic reactions being conducted for FY 2010-2013 [14-17] were summarized and published as three papers in peer reviewed journals. In publication 3, it was shown that behavior of a water molecule at the water-semiconductor interface is fundamentally different from that of a water molecule adsorbed on a semiconductor surface

due to the presence/absence of H-bonds around the water molecule. In publication 2, it was shown that H diffusion at the water-InP interface is significantly higher than that at water-GaP interfaces, and combined with the experimental evidences, it was proposed that facile H diffusion at the water-semiconductor interface might activate additional HER pathways, which, in turn, might enhance overall STH conversion efficiency. An experimental observation consistent with our proposition has been reported on a silicon-based metal-insulator-semiconductor device by Esposito et al. in 2013 [18].

The discovery of potential relevance of H diffusion at the interface led to further development of a novel HER model, which ncorporates the interface diffusion into account (Figure 1). Such a computational model will open up a new design strategy for highly cost-effective photoelectrodes via choice of semiconductor surface treatment which will take full advantage of H diffusion that activates additional HER channels, and via optimal co-catalyst arrangement (for example, minimize use of platinum without sacrificing overall STH conversion efficiency).

In FY 2012, the NREL collaborators have demonstrated that the nitrogen bombardment of GaInP$_2$ photoelectrode surface improves corrosion resistance. In the following year, detailed characterization of the nitrogen treated photoelectrode by the UNLV team led to discovery of un-intentional metal impurities (Pt and Ru), and they are found to be crucial for the improved durability. Accordingly, the focus of SV team shifted from nitrogen alone to separating the role of these impurities. A systematic experimental study on the correlation between corrosion resistance and combination of Pt/Ru/N treatment has been designed by the SV team, and executed by the NREL team [19]. The results have led to a significantly clearer understanding on the extent of correlation between the treatments and the corrosion resistance, however, it also revealed that there are yet to be identified factors that affect corrosion resistance.
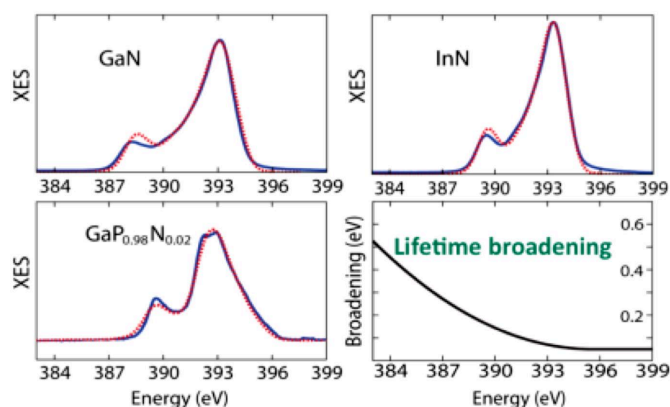

FIGURE 2. Experimental (blue lines) and theoretical (red dash lines) N K-edge XES of three nitride compounds: GaN, InN, and GaP$_{0.98}$N$_{0.02}$, as well as the energy dependent lifetime broadening profile used for the theoretical spectrum.

The SV team is currently in the process of developing a new research plan for precise determination of control parameters for the surface treatment. As a part of this effort, we have been investigating on the N K-edge X-ray emission spectrum (XES) of nitrogen-bombarded GaInP$_2$. In FY 2013, we have established the calculation procedure and identified several nitrogen defect complexes, which are major contributors to the measured spectrum. During this process, we have learned that the experimental XES spectra of InN published in literature show slight disagreement. Since they were critical for calibrating theoretical spectrum, the UNLV team has performed additional measurements on N K-edge XES of high quality InN, GaN, GaP$_{0.98}$N$_{0.02}$ samples provided by the LANL collaborator, Todd Williamson. After careful assessments, theoretical analysis was repeated, and concluded that the FY 2013 results are robust (Figure 2 and 3). We are now in the process of addressing an issue stemming from uncertainty in lifetime broadening, and preparing the draft paper on the characterization of nitrogen impurity states in GaInP$_2$ photoelectrode.
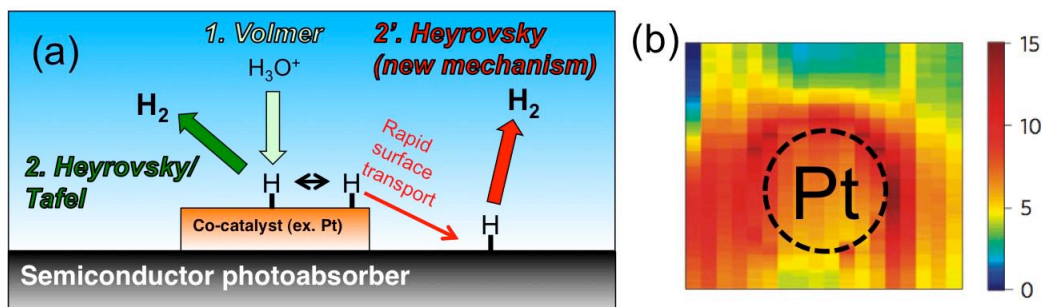

FIGURE 1. (a) Schematics of the novel HER model proposed in the FY 2013 publication 3. In addition to the conventional HER taking place on Pt co-catalyst, facile H diffusion (and reasonably low Heyrovsky barrier) on the semiconductor surface will enable additional HER pathway (red arrow). (b) H$_2$ evolution activity on the Si-based MIS device reported in ref [18]. Pt catalyst (dashed circle) was found to activate HER in surrounding SiO$_2$ surface, which is consistent with our model described in (a). Copyright 2013: Macmillan Publisher Ltd: Nature Material.
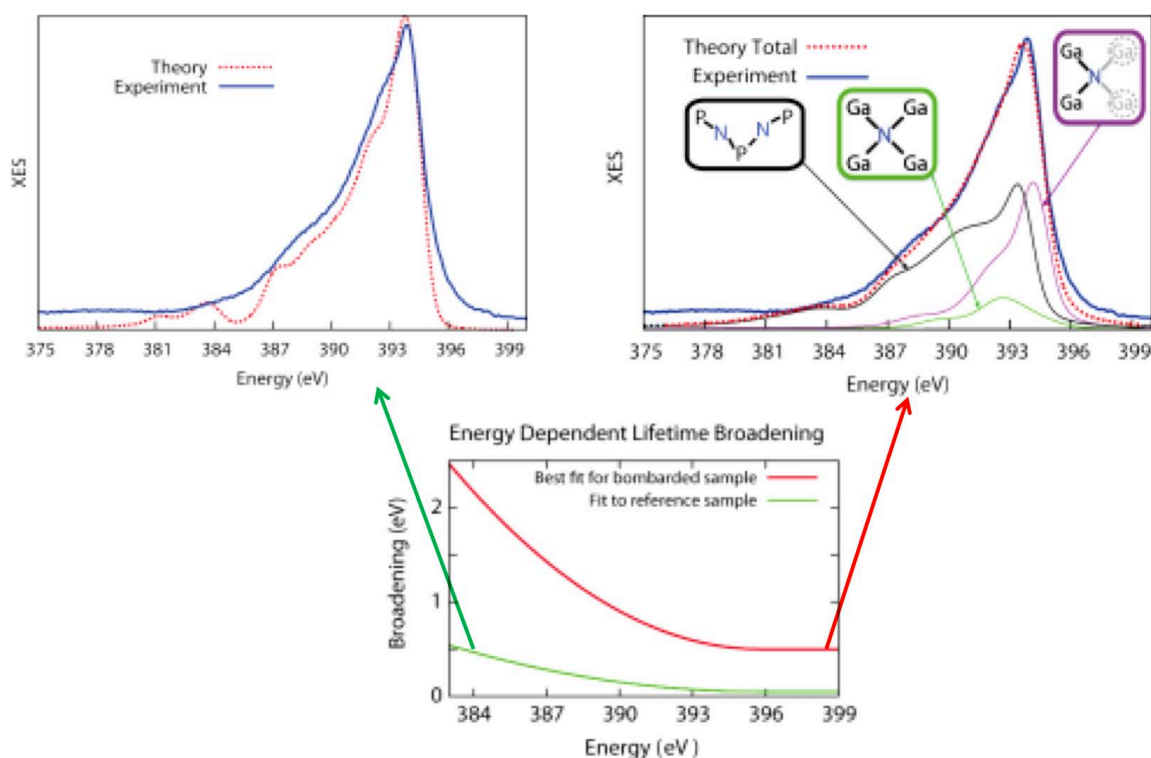
FIGURE 3. Simulated XESs of nitrogen bombarded GaInP$_2$. The left plot was generated with the lifetime broadening used in Figure 2, while in the right plot, the lifetime broadening profile was adjusted so as to obtain the best fit to the UNLV results (blue lines). In general, lifetime of electronic excitation will be decreased by introduction of defects (i.e. larger lifetime broadening), which is expected in the nitrogen bombarded sample used in the UNLV measurements. However, the extent of change in lifetime broadening is not known. Nevertheless, the types of nitrogen defects complex used to generate these theoretical XESs are essentially the same, while the rates of contributions are slightly different.

CONCLUSIONS AND FUTURE DIRECTIONS

- A few potential causes of performance variability problems were identified through the SV team discussions and the PEC literature database development.

- Ab initio study of III-V surfaces and interfaces as well as the development of ab initio-derived Model Hamiltonian for catalyst screening were summarized and published as three papers in peer reviewed journals.

- A novel HER model, which account for H diffusion at the semiconductor-electrolyte interface, has been developed. This model could be used to design a cost-effective PEC electrode, therefore, continuation of the model development is desirable.

- As a part of the SV team, systematic investigation on effective surface treatment for improved electrode durability has been conducted. Unambiguous identification of the control parameters and development of better corrosion mitigation strategy will be the priority for the SV team activity in near future.

SPECIAL RECOGNITIONS & AWARDS/ PATENTS ISSUED

1. 2014 DOE Hydrogen and Fuel Cells Program R&D Award.

FY 2014 PUBLICATIONS/PRESENTATIONS

Publications

1. W.-I. Choi, B.C. Wood, E. Schwegler, and T. Ogitsu, "Site-Dependent Free Energy Barrier for Proton Reduction on MoS$_2$ Edges." J. Phys. Chem. C. **117**, 21772 (2013).

2. B.C. Wood, E. Schwegler, W.-I. Choi, and T. Ogitsu, "Hydrogen-Bond Dynamics of Water at the Interface with InP/GaP(001) and the Implications for Photoelectrochemistry." J. Am. Chem. Soc. **135**, 15774 (2013).

3. B.C. Wood, E. Schwegler, W.-I. Choi, and T. Ogitsu, "Surface chemistry of GaP(001) and InP(001) in contact with water." J. Phys. Chem. C **118**, 1062 (2014).

4. W.-I. Choi, M. Weir, T. Deutsch, T. Williamson, L. Weinhardt, A. Benkert, M. Blum, F. Meyer, M. Bar, K. George, B.C. Wood, D. Prendergast, J. Turner, C. Heske, and T. Ogitsu, "Chemical Envrionment of Implanted Nitrogen Into GaInP$_2$: Characterized with X-ray Emission Spectroscopy." to be submitted.

5. T. Ogitsu, B. Wood, W. Choi, *DOE Fuel Cell Technology Hydrogen Program Annual Merit Review* (2014).

6. Y. Liu, K. Hackenberg, W.-I. Choi, T. Ogitsu, M. Wang, K. Ajayan, B. Yakobson, and B.C. Wood, "Towards surface-active metal dichalcogenides for efficient hydrogen production." submitted.

Presentations

1. Electrochemical Society 224th Meeting, San Francisco, CA, Oct 2013 (one invited, one oral).

2. Invited lecture at Brigham Young University, Provo, UT, Nov 2013.

3. Invited seminar at Rice University, Huston, TX, April 2014.

4. Invited seminar at MIT, Cambridge, MA, May 2014.

5. 2014 Materials Research Society Spring Meeting, San Francisco, CA, April 2014 (poster).

6. DOE Hydrogen and Fuel Cells Program Annual Merit Review, DC, June 2014 (oral).

7. ICMR Workshop on Ab-initio description of charged systems and solid/liquid interfaces for semiconductors and electrochemistry, Santa Barbara, July 2014 (oral).

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