

## II.F.4 Characterization of Materials for Photoelectrochemical (PEC) Hydrogen Production

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- Aid the collaboration partners in the development and modification of novel candidate materials.
- Monitor deliberately introduced modifications of PEC candidate materials in view of the electronic and chemical structure.

### FY 2012 Accomplishments

- Performed non-invasive cleaning procedure using low-energy Ar<sup>+</sup> ion treatment on an air-exposed GaInP<sub>2</sub> film, removing all surface C and most surface O. This process allows determination of the true surface electronic structure including the electronic surface band gap, band edge energies, and the work function.
- Worked with collaborators at NREL to reduce ambient-air-related surface adsorbates to preserve the relevant surfaces for water splitting. Achieved a dramatic reduction in the amount of surface contaminants.
- Used synchrotron-based N K X-ray emission spectroscopy (XES) to determine both the relative amount and the chemical environment of N-treated GaInP<sub>2</sub> films to elucidate differences between effective and ineffective treatments.
- Found good agreement of experimental and theoretical X-ray absorption spectroscopy (XAS) in GaP and InP, in close collaboration with our partners at LLNL.
- In situ gas cell for XES/XAS studies was tested and is operational, a liquid/solid interface electrochemical cell is in development.

### Fiscal Year (FY) 2012 Objectives

Enhance the understanding of PEC materials and interfaces and promote break-through discoveries by:

- Utilizing and developing cutting-edge soft X-ray and electron spectroscopy characterization.
- Determining electronic and chemical structures of PEC candidate materials.
- Addressing materials performance, materials lifetime, and capital costs through close collaboration with the National Renewable Energy Laboratory (NREL) and other partners from the PEC working group.

### Technical Barriers

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

- (Y) Materials Efficiency
- (Z) Materials Durability
- (AA) PEC Device and System Auxiliary Material

### Technical Targets

- Collaborate closely with partners at NREL, Lawrence Livermore National Laboratory (LLNL), and others within the DOE PEC working group to determine the electronic and chemical structure of candidate materials for solar water splitting.



### Introduction

This project is embedded into the Department of Energy's efforts to develop materials for PEC water splitting. If successful, PEC will provide an important route to convert the energy supplied by solar irradiation into a transportable fuel. In order to achieve this goal, suitable materials need to be developed that simultaneously fulfill several requirements, among them chemical stability and optimized electronic structure, both for absorption of the solar spectrum and for electrochemical water splitting at a solid/electrolyte interface. This project experimentally derives the chemical and electronic structure information to (a) judge the suitability of a candidate material, (b) show pathways towards a deliberate optimization of a specific material, and (c) monitor whether deliberate modifications of the material indeed lead to the desired changes in electronic and chemical structure.

## Approach

A unique “tool chest” of experimental techniques is utilized that allows addressing all technical barriers related to electronic and chemical properties of various candidate materials. With these techniques, it is possible to derive surface and bulk band gaps, the energy level alignment at interfaces, the chemical stability of the materials, and the impact of alloying and doping.

The tool chest includes photoelectron spectroscopy with X-ray (XPS [1]) and ultraviolet photoelectron spectroscopy (UPS) excitation to determine the occupied electronic states (core levels and valence electrons), and inverse photoemission spectroscopy (IPES) to determine the unoccupied electronic states. These techniques, performed in the lab at UNLV, are surface-sensitive and allow a detailed determination of the electronic and chemical surface structure. They are complemented by XES and XAS spectroscopy, performed at Beamline 8.0 of the Advanced Light Source, Lawrence Berkeley National Laboratory. XES and XAS also probe the occupied and unoccupied electronic states, but with an increased information depth. Furthermore, they also give insight into the chemical structure, again complementary to the electron-based techniques performed in the lab at UNLV.

## Results

In collaboration with our partners at NREL (T. Deutsch, A. Welch, and J. Turner), we have conducted an investigation of GaInP<sub>2</sub> thin film surfaces. Results were immediately shared with the collaboration partners and discussed in detail through PowerPoint presentations, at phone conferences, and working group meetings. Among the multitude of data obtained, this report focuses on the ion treatment and other methods to remove or reduce surface contamination, so that the underlying electronic structure of the “true” GaInP<sub>2</sub> surface can be determined and used as a benchmark for the study of surfaces exposed to controlled environments (including air, oxygen, and water/electrolyte). Further results, including the N K XES spectra and the comparisons of experimental and theoretical XAS spectra for GaP and InP, are shown in the annual review presentation (the theoretical work was performed by our partners at LLNL).

The surface sensitivity of XPS implies that small amounts of C and O at the surface can have a large effect on the apparent (as-measured) electronic structure (i.e., surface adsorbates attenuate the underlying relevant electronic structure of GaInP<sub>2</sub>). Therefore, a low-energy (50 eV) Ar<sup>+</sup> ion treatment series was performed to remove these contaminants without altering the GaInP<sub>2</sub> surface, thereby revealing the relevant electronic structure of the active PEC material. Note that this treatment is quite different from conventional “sputter-cleaning”, in which significantly higher ion energies (500 to 5,000 eV) have to be used.

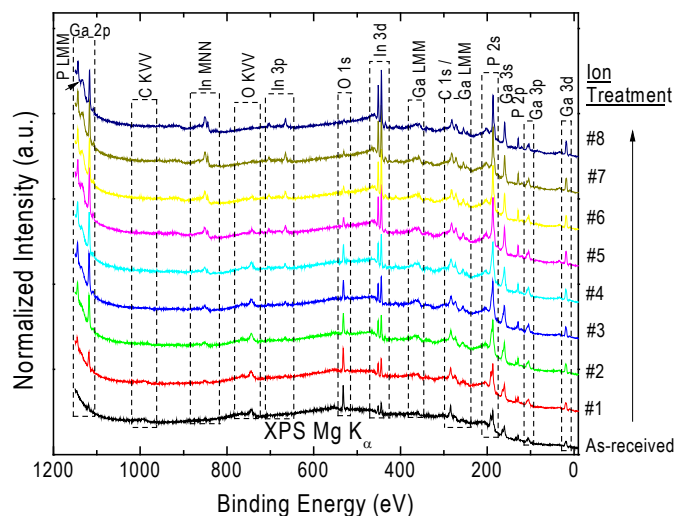
Table 1 lists the exposure times for each treatment (as well as the cumulative treatment time) of this series.

**TABLE 1.** Exposure Times for Each Low-Energy Ion Treatment

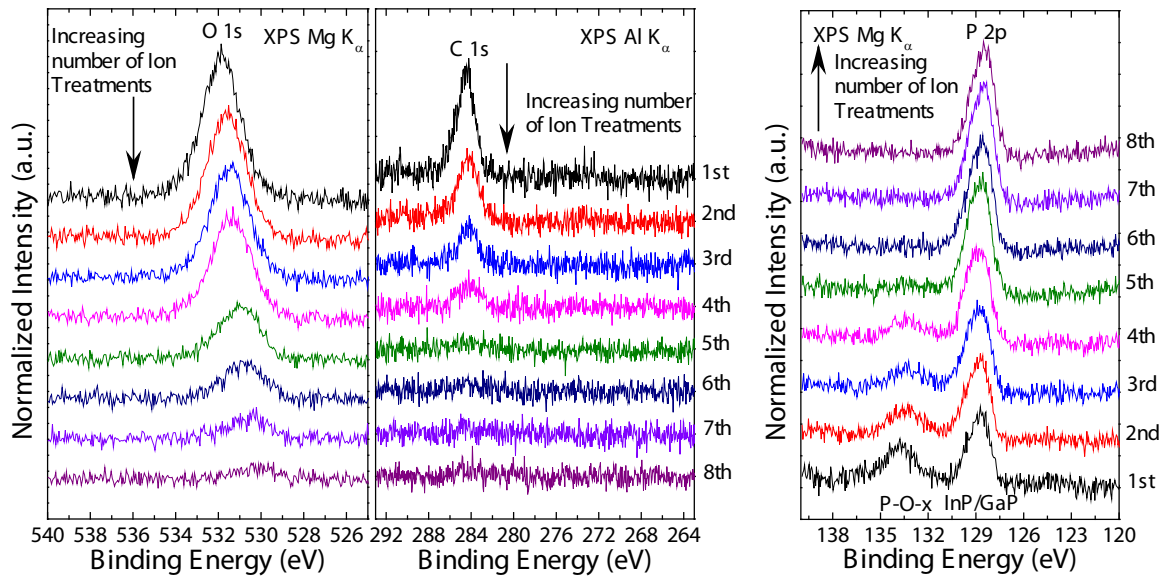
Treatment Number	Length of Time Under 50 eV Ar <sup>+</sup> Ion Treatment	Cumulative Time Under 50 eV Ar <sup>+</sup> Ion Treatment
As Received	0	0
1	15 minutes	15 minutes
2	30 minutes	45 minutes
3	30 minutes	75 minutes
4	1 hour	135 minutes
5	2 hours	255 minutes
6	2 hours	375 minutes
7	2 hours	495 minutes
8	4 hours, 30 minutes	765 minutes

As a first step, we examine the Mg K<sub>α</sub> XPS survey spectra for this ion-treatment series, as shown in Figure 1. The spectra are normalized to the same background and offset for visibility. Most notable here is the increase of the various Ga, In, and P signals, while both C and O decrease as a function of treatment time. The surface contaminants are clearly being removed, and no longer attenuating the signal from the underlying film of interest.

Further surface analysis is based on selected detail spectra, as displayed in Figure 2. In the O 1s region, we note that the O signal does not simply decrease with increasing ion treatments, but also shifts toward lower binding energy. This change is likely the result of two separate O species on the film, one of which is both more abundant and more



**FIGURE 1.** XPS Mg K<sub>α</sub> survey spectra of a single GaInP<sub>2</sub> thin film sample after various low-energy Ar<sup>+</sup> ion treatment steps, as listed in Table 1. Spectra were normalized to the background and offset for visibility.

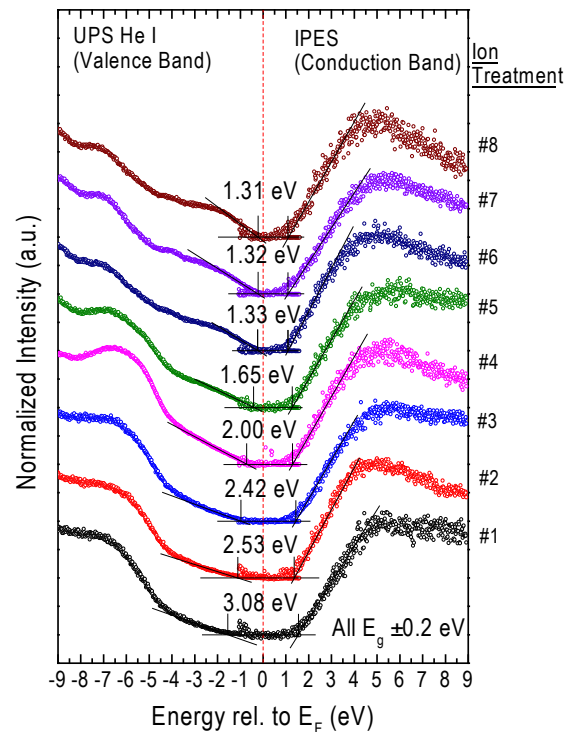


**FIGURE 2.** XPS detail spectra of the O 1s ( $Mg K_{\alpha}$ ), C 1s ( $Al K_{\alpha}$ ) and P 2p ( $Mg K_{\alpha}$ ) regions of the  $GaInP_2$  thin film during the low-energy  $Ar^+$  ion treatment. Spectra were normalized to the background and offset for visibility. Changes in the spectra mirror the surface concentrations of the respective species.

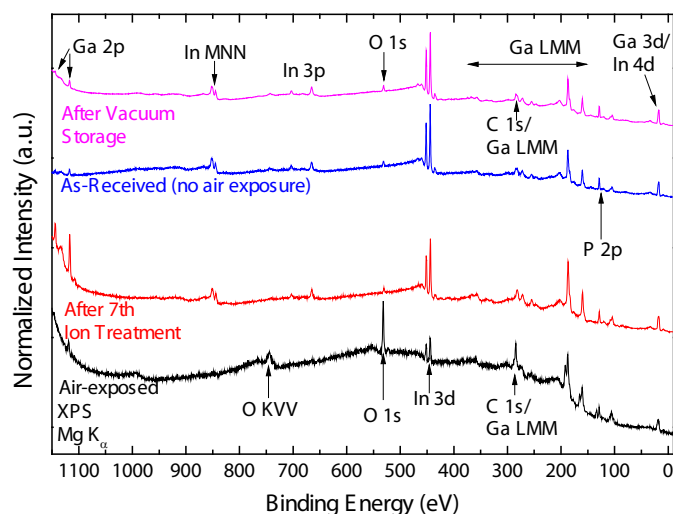
easily removed with ion treatment. The O signal is not fully removed, in contrast to the C signal, which becomes indistinguishable from the background starting at the 5<sup>th</sup> treatment step. The P 2p spectra clearly show two different P species, one associated with the  $GaInP_2$  film ( $\sim 128$  eV) and one at higher binding energy ( $\sim 134$  eV) with a surface oxide that is removed with ion treatment.

One of the most powerful and unique abilities in our “tool chest” is the use of UPS to measure the valence band and the use of IPES to derive the corresponding information for the conduction band [2]. These two techniques can be combined to determine the electronic surface band gap, as shown in Figure 3. Simultaneous optimization of the two band edge positions (with respect to the Fermi energy) and the band gap is essential for PEC materials - all three can be derived from these measurements and are indicated with vertical lines (for the band edges) and numerical values (for the band gap) in Figure 3. The band gap narrows with successive ion treatments, largely due to the valence band maximum shifting towards the Fermi energy with treatment time. Since the bulk band gap for  $GaInP_2$  is 1.75 eV, as compared to the final electronic surface band gap of 1.31 eV, we ascribe this difference to an ion-induced modification of the electronic surface structure (beyond the simple removal of surface adsorbates), which strongly indicates the need for optimal surface preservation between growth and characterization, so that the need for additional surface cleaning steps is minimized.

We have thus worked with our collaborators at NREL to eliminate air exposure of the  $GaInP_2$  films between growth and characterization. For this purpose, John Geisz and Waldo



**FIGURE 3.** UPS (left) and IPES (right) of the  $GaInP_2$  thin film during low-energy  $Ar^+$  ion treatment. Both spectra were calibrated to the Fermi energy of a Au reference sample to align energy scales. Drawn lines indicate either the valence band maximum (UPS) or conduction band minimum (IPES) and are used to determine the band gap.



**FIGURE 4.** XPS Mg  $K_{\alpha}$  survey spectra of two GaInP<sub>2</sub> thin films with modified sample handling. The first film is shown before (black) and after (red) low-energy Ar<sup>+</sup> ion treatment while the second is shown as received (blue) and after storage in UHV (magenta).

Olavaria (NREL) attached an N<sub>2</sub>-purged glove bag to their synthesis reactor and removed the sample into this glove bag where it was packaged using a vacuum seal device. At UNLV, the package was opened in a N<sub>2</sub> glove box and introduced to ultra-high vacuum (UHV) for analysis.

While the analysis of this sample is still ongoing, Figure 4 demonstrates the effectiveness of this change in sample handling. Mg  $K_{\alpha}$  XPS survey spectra are shown for the above-discussed ion-treated sample, both as-received and after the 7<sup>th</sup> ion-treatment step, while the newer sample is plotted as-received and after a few weeks of storage in UHV. The differences in the films are most apparent for the significantly reduced C 1s (~285 eV) and O 1s (~530 eV) signals and the significantly increased In and Ga signals (comparable to those after the 7<sup>th</sup> ion treatment). We expect this cleaner starting point to allow us to reach our goal of measuring the “benchmark” electronic structure of GaInP<sub>2</sub> films.

## Conclusions and Future Directions

### Conclusions

- Successfully maintained operations of our multi-chamber UHV spectroscopy.
- Conducted experiments with our partners at NREL and select partners of the DOE PEC working group, in particular focusing on the establishment of suitable surface-cleaning procedures of GaInP<sub>2</sub> thin films and the analysis of their electronic and chemical surface properties.

- Conducted experiment-theory comparisons of XAS spectra of GaP and InP, together with our theory partners at LLNL.
- In situ gas cell tested and operational, liquid/solid interface electrochemical cell for XES/XAS studies in development.

### Future Directions

- We will determine the benchmark electronic and chemical properties of GaInP<sub>2</sub> thin film surfaces as a baseline and will study the impact of controlled surface exposures (air, oxygen, water/electrolyte) on these characteristics.
- We will further correlate our results with theoretical calculations from our partners at LLNL, extending these activities to XES measurements as well.
- We will continue our development of a liquid/solid interface electrochemical cell for XES/XAS studies.

## FY 2012 Publications/Presentations

1. “What electronic structure should a PEC device have (and can we measure it)?”, C. Heske, SPIE Optics & Photonics Conference, San Diego, August 12–16, 2012 (invited oral).
2. “Electronic surface structure of GaInP<sub>2</sub> Thin Films used for Photoelectrochemical Water Splitting”, K. George, M. Weir, S. Krause, I. Tran, K. Horsley, M. Blum, L. Weinhardt, C. Heske, T. Deutsch, J. Turner, T. Ogitsu, B. Wood, R. Wilks, M. Baer, and W. Yang, Symposium on Materials for Catalysis in Energy, Materials Research Society Spring Meeting, April 2012 (contributed oral).
3. “Passivation of Photoelectrochemical Water Splitting Electrodes Based on III-V Compound Semiconductors via Surface Nitridation”, T. Deutsch, A. Welch, A. Lindeman, M. Baer, L. Weinhardt, M. Weir, K. George, C. Heske, and J. Turner, Symposium on Materials for Catalysis in Energy, Materials Research Society Spring Meeting, April 2012 (contributed oral).
4. “Using soft x-rays to look into (buried) interfaces of energy conversion devices”, C. Heske, Department of Physics, Northern Arizona University, February 28, 2012 (invited oral).
5. “Spektroskopie der elektronischen Struktur von Grenzflächen in Solar- und anderen Zellen”, C. Heske, Zentrum für Sonnenenergie- und Wasserstoff-Forschung Baden-Württemberg (ZSW), Stuttgart, February 15, 2012 (invited oral).
6. “How can a synchrotron help to make solar devices better?”, C. Heske, Institute for Chemical Technology and Polymer Chemistry (ITCP), Karlsruhe Institute of Technology (KIT), Nov. 25, 2011 (invited oral).
7. “Wie man mit weicher Röntgenstrahlung die lokale chemische Umgebung ausspäht”, C. Heske, Institute for Technical Chemistry - Thermal Waste Treatment Division (ITC-TAB), Karlsruhe Institute of Technology (KIT), Nov. 23, 2011 (invited oral).

## References

1. D. Briggs and M. P. Seah, *Practical Surface Analysis*, John Wiley and Sons, Chichester, 1990.
2. M. Baer, L. Weinhardt, B. Marsen, B. Cole, N. Gaillard, E. Miller, and C. Heske, *Appl. Phys. Lett.* **96**, 032107 (2010).
3. M. Baer, S. Nishiwaki, L. Weinhardt, S. Pookpanratana, O. Fuchs, M. Blum, W. Yang, J.D. Denlinger, W.N. Shafarman, and C. Heske, *Appl. Phys. Lett.* **93**, 244103 (2008).