

## II.G.5 Characterization of Materials for Photoelectrochemical Hydrogen Production

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### Technical Targets

- Collaborate closely with partners within the DOE PEC working group to determine the electronic and chemical structure of candidate materials for solar water splitting.
- Aid the collaboration partners in the development/modification of novel candidate materials.
- Monitor deliberately introduced modifications of PEC candidate materials in view of the electronic and chemical structure.

### Accomplishments

- Further studies of the impact of Mo doping/alloying in  $\text{WO}_3:\text{Mo}/\text{WO}_3$  bilayer structures (with University of Hawaii/Hawaii Natural Energy Institute).
- Investigation of the band gap of a-SiC and its change after surface treatments (with MVSystems).
- Studies of PEC-tested and untested  $\text{CuGaSe}_2$  samples (with University of Hawaii/Hawaii Natural Energy Institute and NREL).
- Completion of  $\text{Fe}_2\text{O}_3$  thin film analysis (with University of California, Santa Barbara).



### Objectives

Enhance the understanding of photoelectrochemical (PEC) materials and interfaces and promote breakthrough 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 partners from the PEC working group.

### Technical Barriers

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

- (H) System Efficiency
- (K) Durability
- (G) Capital Cost

### 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 to address all technical barriers

related to electronic and chemical properties of various candidate materials. With these techniques it is possible to measure 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) and ultraviolet excitation to determine the occupied electronic states (core levels and valence electrons) and inverse photoemission to determine the unoccupied electronic states. These techniques, performed in the lab at UNLV, are surface-sensitive and allow a complete determination of the electronic and chemical *surface* structure. They are complemented by X-ray emission (XES) and X-ray absorption (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 a larger 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, we have investigated numerous sample series on a variety of PEC candidate materials. Results are immediately shared with the collaboration partners and discussed in detail through powerpoint presentations, at phone conferences, and working group meetings. In the brevity of this report, we will focus on one materials class only, namely copper gallium diselenide (CGS) samples grown at the University of Hawaii and PEC-tested at NREL. Results for other material classes (tungsten trioxide, amorphous silicon carbide, and iron oxide) are shown in the annual review presentation.

To demonstrate the chemical insights that can be gained with our experimental tool chest (complementary to the electronic structure information described in last year's report for, e.g.,  $\text{WO}_3$  thin films), we will focus on five samples as described in Table I.

Figure 1 shows Se M-edge and S L-edge XES spectra of the CGS samples and of  $\text{CdSO}_4$  (top spectrum) and  $\text{Cu}_2\text{Se}$  (bottom spectrum, showing a significant Se oxidation and sulfate contamination) references. Sample A (untested CGS) shows a dominant Se  $M_{2,3}$  emission line at 143 eV and some weaker features at higher emission energies (three peaks from 152 to 157 eV and one broad peak around 162 eV). The latter are indicative of Se oxide formation and show that the untested CGS sample is weakly oxidized. In contrast, the emission spectrum of Sample B (CGS in  $\text{H}_2\text{SO}_4$  electrolyte for 24 hours) is dominated by the sulfate and/or selenium oxide features. The sulfate formation is likely from residual sulfuric acid on the surface of the samples, while selenium oxide formation

TABLE I. CGS samples

Name in report	Sample Identification	Test parameters
A	CGS 090202-13 4	control
B	CGS 5	In 0.5M $\text{H}_2\text{SO}_4$ for 24 hr in dark
C	CGS 090202-22 1	Illuminated OCP, 0.5M $\text{H}_2\text{SO}_4$ , 2 fiber optic illuminators, 60 s: 20 dark, 20 light, 20 dark
D	CGS 090202-22 2	3E Chopped light IV, 0.5M $\text{H}_2\text{SO}_4$ , AM1.5, -1.0 V vs. Ref to 0.05 vs. open circuit, chop every 100 mV
E	CGS 090202-13 3	Illuminated OCP, 2E: -2.5 V to 0.05, 3E IV: -1 V to 0.05 V, performed in this order

OCP - open circuit potential

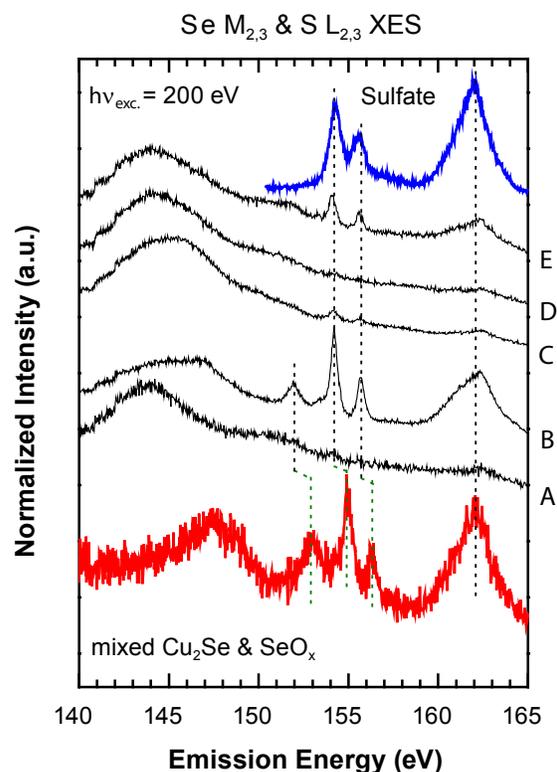


FIGURE 1. Se  $M_{2,3}$  and S  $L_{2,3}$  XES spectra of samples A–E with reference spectra of  $\text{CdSO}_4$  (top) and  $\text{Cu}_2\text{Se}$  (bottom, showing a significant Se oxidation or sulfate contamination). Dashed lines indicate sulfate and selenium oxide features.

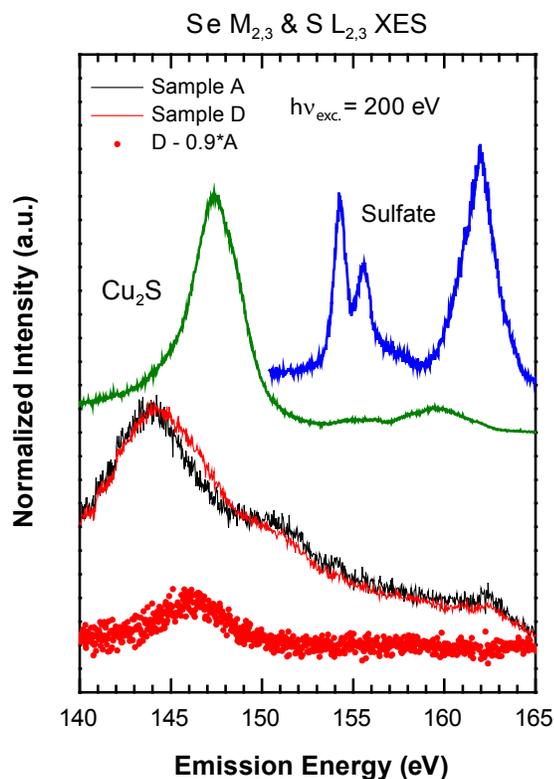
is likely due to the CGS exposure to the aqueous sulfuric acid solution. Note that the cross section for S  $L_{2,3}$  emissions is significantly larger than that for Se  $M_{2,3}$  emission, and thus the observed features are more likely due to sulfate deposition.

The spectra of samples C–E at first glance appear to be similar to that of sample A, but upon closer

inspection significant differences are visible. In particular, the sulfate/selenium oxide peak intensity increases in the order D–C–E.

Additional analysis was performed on the spectrum of sample D in Figure 2 by subtracting the spectrum of sample A (weighted by 0.9) to account for the signal originating from the CGS substrate (difference spectrum shown in red). The difference spectrum is characteristic of sulfur emission (specifically sulfide) with a dominant peak at 146 eV. This suggests that a new sulfur-containing species is present on the surface of the tested sample. Note that this is not a sulfur oxide species, because the characteristic features at emission energies above 153 eV, are notably absent in the difference spectrum. As one possibility, we note that the difference spectrum is similar to that of a copper sulfide (e.g.,  $\text{Cu}_2\text{S}$ , shown in the same figure, in green), but other sulfides might also play a role.

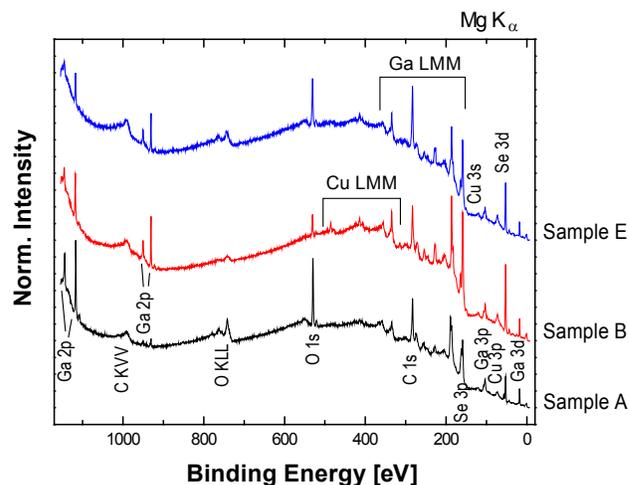
We thus find that the PEC testing influences the local Se environment at the surface. Additionally, we are able to detect S atoms adsorbed onto the CGS surface after PEC testing, in some cases as a sulfide and in others as a sulfur oxide. We find that the chemical structure of the samples (with respect to the local Se and S environments) varies between samples, and thus allow correlation with the PEC test parameters that were used.



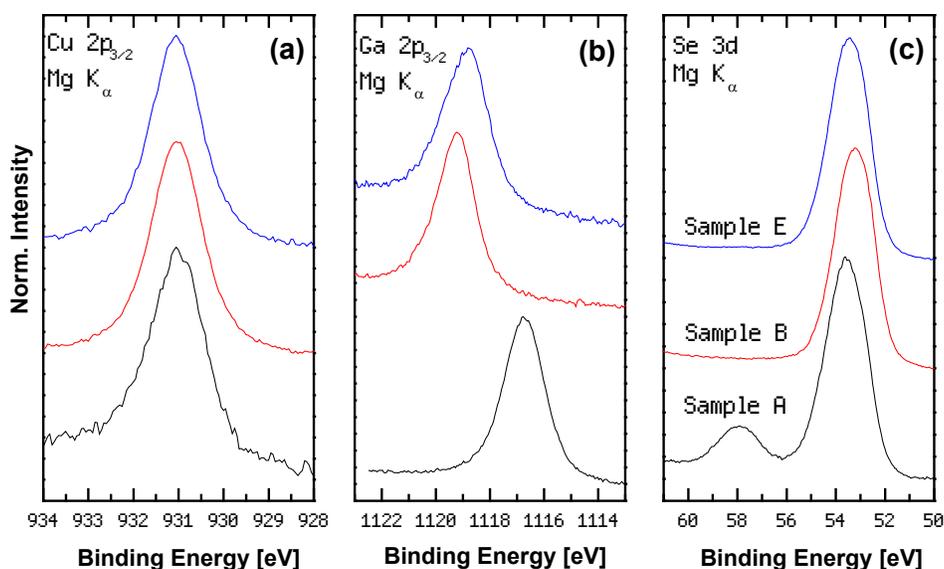
**FIGURE 2.** XES spectra of samples A and D, as well as difference spectrum resulting from  $D - 0.9 \cdot A$  (along with  $\text{Cu}_2\text{S}$  and sulfate reference spectra).

The CGS samples described in Table I were also investigated with XPS at the UNLV lab to elucidate the chemical surface composition after testing. Survey scans of the three samples are shown in Figure 3. In the control sample A, copper, gallium, and selenium are observed (as expected). Significant surface contamination is also found, as indicated by the presence of oxygen and carbon. For the tested samples B and E, the same five elements are detected, but their relative intensities differ. For sample B, the signals ascribed to copper and selenium are enhanced, while the oxygen signal has decreased when compared to the control sample A. Sample E has similarly increased signals of copper and selenium, but the oxygen has decreased much less. Thus, even just based on the survey spectra, a qualitative comparison between the different tested and non-tested samples already reveals significant changes in surface composition.

Detailed spectra (with a smaller energy range and better resolution) of Cu, Ga, and Se core levels were acquired to monitor the chemical changes of the CGS surface as a function of PEC testing. In Figure 4a, the Cu  $2p_{3/2}$  region of all three samples is shown. The peak shape and energetic position of samples B (tested in dark) and E (tested in light) are very similar to that of sample A (untested). Although the copper signal in samples B and E has increased, the copper present on the surface of all three samples appear to be in the same chemical environment. In contrast, the Ga  $2p_{3/2}$  region (Figure 4b) of the untested sample (A) and the tested samples (B and E) are all at different binding energies. The tested samples are at higher binding energies (at about 1,119 eV), while the untested sample is at about 1,117 eV. The Ga  $2p_{3/2}$  (energetic) position of the tested samples is in agreement with reported  $\text{Ga}_2\text{O}_3$  values [1]. At first glance, the tested samples (B and E) appear to be similar to each other, but upon



**FIGURE 3.** XPS survey spectra of CGS samples A (control), B (tested in dark), and E (tested under illumination).



**FIGURE 4.** XPS spectra of (a) Cu 2p<sub>3/2</sub>, (b) Ga 2p<sub>3/2</sub>, and (c) Se 3d. Sample A, B, and E are shown at the bottom (black), center (red), and top (blue), respectively

closer inspection, the spectral width of sample E is wider than that of sample B, and the peak maximum of sample B is at slightly higher binding energy. This is an initial indicator that the gallium on the surface of sample E may be in two different chemical environments, one of them possibly identical to that of sample B. We thus find that the details of PEC testing (in particular, dark vs. illuminated) do affect the chemical Ga environment on the surface. In the case for Se, the main peak (at about 53.5 eV) positions are about the same for all three samples. However, the untested sample (A) has an additional peak at higher binding energies which is in agreement with literature values of Se 3d in SeO<sub>2</sub> chemical environments [1], and which has also been previously found by our group on Cu(In,Ga)Se<sub>2</sub> surfaces [2]. This additional peak is absent in the tested samples. This absence could be due to the acid exposure of the samples, which etched away the oxide Se surface atoms.

From XPS, we thus find that the PEC testing influences the local chemical environment of the Se and Ga atoms at the surface. Such results give valuable insights into the atomic-scale effects on PEC candidate material surfaces under operating conditions and will contribute to a guided search for custom-tailored stable PEC materials.

## Conclusions and Future Directions

In conclusion, development of the spectroscopic “tool chest” to give a comprehensive picture of the electronic and chemical structure has become a key component of the DOE PEC research and development efforts. Evaluating a variety of PEC candidate materials in view of their electronic and chemical properties has

enhanced progress in many of the DOE PEC working group projects. Continued experiments within excellent collaboration structures with a large number of partners of the DOE PEC working group has been critical to recent progress, and is vital to future success in meeting DOE targets. As a result, future directions include:

- Continue the collaborations with our existing partners and bring new partners “on board”.
- Continue to determine electronic and chemical properties of various PEC candidate materials manufactured by the collaboration partners within the DOE PEC working group.
- Continue to improve the currently available experimental approaches.

## FY 2010 Publications/Presentations

1. “Mo incorporation in WO<sub>3</sub> thin film Photoanodes – Tailoring the electronic structure for photoelectrochemical hydrogen production”, M. Bär, L. Weinhardt, B. Cole, B. Marsen, N. Gaillard, E.L. Miller, and C. Heske, *Appl. Phys. Lett.* **96**, 032107 (2010).
2. “REVIEW: Accelerating materials development for photoelectrochemical hydrogen production: Standards for methods, definitions, and reporting protocols”, Z. Chen, T.F. Jaramillo, T.G. Deutsch, A. Kleiman-Shwarscstein, A. Forman, N. Gaillard, R. Garland, K. Takanabe, C. Heske, M. Sunkara, E.W. McFarland, K. Domen, E.L. Miller, J.A. Turner, and H.N. Dinh, *J. Mater. Res.* **25**, 3-16 (2010).
3. “Origin of improved current collection in WO<sub>3</sub>/WO<sub>3</sub>:Mo bilayer photoelectrodes”, N. Gaillard, B. Cole, B. Marsen, J. Kaneshiro, E.L. Miller, L. Weinhardt, M. Bär, C. Heske, K.-S. Ahn, Y. Yan, and M.M. Al-Jassim, *J. Mater. Res.* **25**, 45-51 (2010).

4. “X-ray and electron spectroscopy studies of oxide semiconductors for photoelectrochemical hydrogen production”, C. Heske, L. Weinhardt, and M. Bär, Chapter 6 of “On Solar Hydrogen & Nanotechnology”, ed. L. Vaysieres, Wiley & Sons, Singapore, January 2010 (ISBN 978-0-47082-397-2).
5. Kyle George, Masters Thesis, UNLV, December 2009: “Characterization of Fe<sub>2</sub>O<sub>3</sub> Thin Films for Photoelectrochemical Hydrogen Production.”
6. “Chemical and electronic structure of a-SiC thin films for photoelectrochemical water splitting”, Y. Zhang, K. George, S. Pookpanratana, T. Hofmann, M. Blum, M. Bär, C. Heske, L. Weinhardt, J. Hu, F. Zhu, A. Madan, W. Yang, and J.D. Denlinger, SPIE Optics + Photonics Conference, San Diego, Aug. 2 – 6, 2009 (oral).
7. C. Heske, “Using soft x-rays and electrons to determine the electronic structure of materials for photoelectrochemical water splitting”, 26<sup>th</sup> European Conference on Surface Science (ECOSS 26), Parma, Italy, Aug. 30 – Sept. 4, 2009 (invited).
8. “Using soft x-rays to look into (buried) interfaces of energy conversion devices”, Chemistry and Geochemistry Department at the Colorado School of Mines, Golden, CO, September 25, 2009 (invited).
9. C. Heske, “Soft x-ray and electron spectroscopy of the electronic structure of water and materials for photoelectrochemical water splitting”, 3<sup>rd</sup> Horiba & 11th ISSP International Symposium on “Hydrogen and Water in Condensed Matter Physics”, Simeinomori, Chiba, Japan, October 12–16, 2009 (invited).
10. “Using soft x-rays to look into interfaces of energy conversion devices”, Materials Science & Engineering Colloquium (co-sponsored by ECE and Physics), Boston University, December 4, 2009 (invited).
11. “How x-ray and electron spectroscopies can help to tackle the energy problem”, Physics Department, Free University Berlin, Germany, January 20, 2010 (invited).
12. “Characterization of Fe<sub>2</sub>O<sub>3</sub> Thin Films for Photoelectrochemical Hydrogen Production”, K. George\*, 2010 Southern Nevada Math & Science Conference (Southern Nevada Science Teachers Association), Las Vegas, Jan. 23, 2010 (oral).
13. “Using soft x-rays to look into (buried) interfaces of energy conversion devices”, Department of Physics, Technical University of Denmark, March 12, 2010 (invited).
14. “Here Comes the Sun! Energizing the Future with Electrons, Photons, and Innovation”, Keynote Address, Future of the Future Symposium, Arizona Western College, Yuma, AZ, March 18, 2010 (invited).
15. C. Heske, “Using soft x-rays to look into interfaces of photoelectrochemical devices”, Symposium on Synchrotron and Neutron Techniques for Energy Materials Research, Materials Research Society Spring Meeting, San Francisco, April 5–9, 2010 (invited).

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