

Soft X-ray emission spectroscopy of the liquid-solid interface between water and a Cu(In,Ga)(S,Se)₂ thin film solar cell absorber

C. Heske¹, U. Groh¹, O. Fuchs¹, L. Weinhardt¹, E. Umbach¹, Ch.-H. Fischer², Th. Schedel-Niedrig², M.Ch. Lux-Steiner², S. Zweigart³, F. Karg³, J.D. Denlinger⁴, B. Rude⁴, C. Andrus⁵, and F. Powell⁵

¹Experimentelle Physik II, Universität Würzburg, Am Hubland, D-97074 Würzburg, Germany

²Hahn-Meitner-Institut, Glienicker Str. 100, D-14109 Berlin, Germany

³Siemens & Shell Solar GmbH, SSSG T, Otto-Hahn-Ring 6, D-81739 München, Germany

⁴Advanced Light Source, 1 Cyclotron Rd., Berkeley, CA 94720

⁵Luxel Corp., 515 Tucker Ave., Friday Harbor, WA 98250

INTRODUCTION

The development of experimental methods to probe the properties of liquid-solid interfaces is one of the fundamental issues for understanding a multitude of natural and technological processes involving liquids. Up to date, however, very few experiments have been performed to learn about the electronic structure, particularly if an atom-specific point of view is desired. While in surface science such information can easily be derived from photoelectron spectroscopy, this approach is not viable for the study of liquid-solid interfaces due to the limited information depth of PES. Thus, the necessity to probe "through" a liquid (or solid) layer calls for photon-in-photon-out experiments. The soft X-ray regime, however, which is the most suitable to study core and valence states of light elements, has not yet been explored, mostly due to the high attenuation of soft X-rays in matter. In this report we demonstrate that soft X-ray emission spectroscopy (XES) can be used to investigate the chemical and electronic properties of particular atoms at liquid-solid interfaces, in this case the water–Cu(In,Ga)(S,Se)₂ interface. Furthermore, we will show that, with XES, it is possible to monitor interfacial chemical reactions with high spectral resolution *in-situ*.

MATERIAL SYSTEM

Cu(In,Ga)(S,Se)₂ (CISSe) is widely used as an absorber material in thin film solar cells, and conversion efficiencies up to 18.8 % have been achieved [1]. Apart from being a model system for the present investigation, the water–CISSe interface is of large importance for two reasons. First, a complete CISSe solar cell is comprised of several thin film layers, including the CISSe absorber layer and a thin (approx. 20 nm) CdS buffer deposited in a chemical *bath* deposition process. The CdS/CISSe interface plays one of the central roles in understanding the electronic structure of the devices. Hence, the possibility to study liquid-solid interfaces *in-situ* allows the monitoring of the substrate, the growing film, and the interface formation process from a spectroscopic point of view. Secondly, one of the main issues on the way to a complete industrial product is the control of humidity impact on the electronic cell properties. The investigation of the relevant water–solid interfaces is expected to shed light on the chemical and electronic changes induced by the humidity on an accelerated time scale.

EXPERIMENTAL

High-resolution soft X-ray emission spectroscopy was performed at beamline 8.0 utilizing the SXF endstation. Beamline 8.0 allows experiments with an excitation photon flux of about 4 x

10^{15} photons/sec near the sulfur $L_{2,3}$ edge. Thin films of CISSe were prepared in a rapid thermal process of elemental precursor layers on Mo-coated soda-lime glass in a sulfur-containing environment. The experiments were performed in ultra-high vacuum (UHV) utilizing suitably designed stainless steel liquid cells, which were glued to the CISSe sample surface with a UHV-compatible epoxy. In the design of the liquid cells, a channel of $1.3 \mu\text{m}$ of liquid water was created between the CISSe surface and a $1 \mu\text{m}$ -thick polyimide (PI) window. After hardening of the epoxy (approx. 24 hours), the complete assembly was transferred into UHV for experiments. Reference experiments were also conducted on "bare" CISSe films as well as on PI/Vacuum/CISSe sandwich structures.

RESULTS

Fig. 1 presents a set of sulfur $L_{2,3}$ emission spectra obtained by excitation well above the absorption edge ($h\nu = 200 \text{ eV}$). The bottom spectrum was obtained from the "bare" CISSe film surface, i.e., taken directly from the solar cell production line. Peak (1) stems from the emission of sulfur atoms bound in a sulfide environment, and is due to photons emitted by filling S 2p core holes with S 3s electrons [2]. Peaks (2) are associated with the same electronic transition, but for sulfur atoms bound to oxygen. In the present case, the absence of an additional peak around

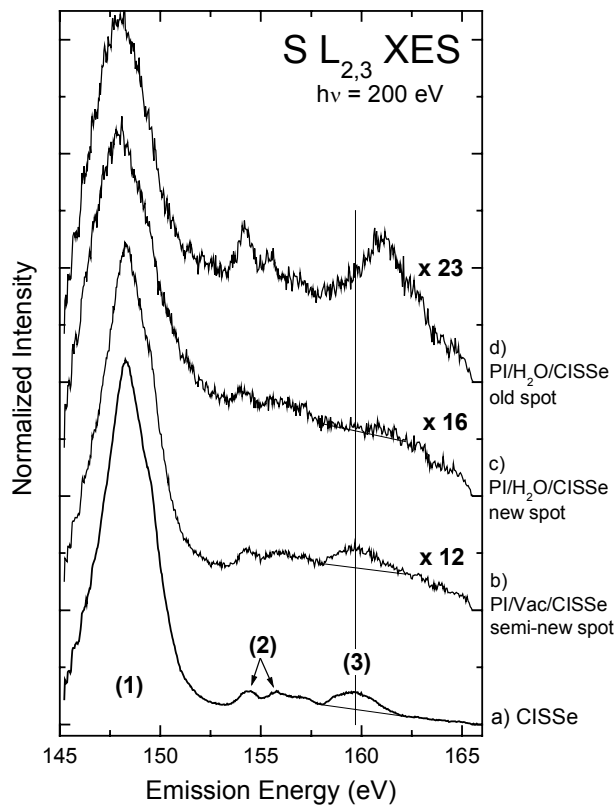


Figure 1. $S L_{2,3}$ X-ray emission spectra of a $\text{Cu}(\text{In,Ga})(\text{S,Se})_2$ (CISSe) thin film solar cell absorber film (a) taken from the production process, (b) seen through a $1 \mu\text{m}$ polyimide (PI) window, and under an additional $1.3 \mu\text{m}$ water layer (c: new sample spot, d: old sample spot). Samples "under water" show a reduced intensity of the S-Cu-bond and, after X-ray exposure, a sulfate formation.

161.1 eV indicates that at most two oxygen atoms are bound to each probed sulfur atom. The broad peak (3) is due to Cu 3d states in the upper valence band of CISSe and, because of the local nature of the excitation, is indicative of sulfur-copper bonds. In short, the spectral features of the sulfur XES spectrum give a wealth of detailed information about the local chemical bond of the sulfur atoms, which can now be used to monitor interfacial processes.

As indicated in Fig. 1 by the magnification factors at the right hand side, the observed signal intensity is reduced by both the PI window as well as the liquid water layer. These attenuation factors indicate the necessity to use high-flux excitation from a third generation synchrotron source. Note that the PI window is damaged by extended exposure to X-rays. Thus, the transmission decreases as a function of exposure within the probed area, and hence the "age" of the spot also factors into the signal attenuation. The "age" of the different spectra is given on the right-hand side of Fig. 1. A closer inspection of spectra a) and b) reveals that no changes are observed for the PI/Vacuum/CISSe sample (as expected). However, we find a reduction of the intensity associated with sulfur-copper

bonds (peak 3) due to the 24 hour storage "under water" (spectrum c). An even more pronounced spectral change is observed after exposure to X-rays (30 min, spectrum d). Based on the strong S 3d-related emission at 161.1 eV, this spectral change is interpreted as a sulfate formation at the water/CISSe interface.

Apart from a detailed look at the chemical and electronic environment of sulfur atoms, also the Na K_{α} emission line proves to be a helpful tool to monitor the interfacial reaction at the water/CISSe interface. Na-assisted growth has been shown to substantially improve the efficiency of the CISSe solar cells. Until today, the impact of the Na has not been fully clarified, mostly because several enhancing mechanisms have been proposed and because, due to the complexity of the system, these different mechanisms are not easily separable. An established model by Kronik et al. [3] suggests an interaction of sodium and oxygen at the CISe surface. Nevertheless, apart from a co-adsorption study in ultra-high vacuum [4], no direct experimental evidence of a chemical interaction between sodium and oxygen has yet been reported. Such a direct correlation can now be derived from a simultaneous recording of Cu L_{α} and Na K_{α} XES spectra. As expected, we find a small Na signal on the CISSe surface, which does not change in intensity for the PI/Vacuum/CISSe sample. Also, the 24-hour storage under water only leads to a small increase. In contrast, when exposing the sample to the soft X-ray beam, we find a dramatic increase of the Na content at the interface in the course of time, in parallel with the above-discussed surface oxidation (sulfate formation). Apparently, the possibility to form a sulfate species attracts Na atoms from the CISSe film towards the surface. Here, the original driving force could be the X-ray-induced creation of O^{2-} and/or OH^{-} ions, which then react with the CISSe surface and alter the free energy, such that Na atoms diffuse to the water/CISSe interface. Also the opposite process, namely that the X-ray excitation attracts Na atoms to the surface (e.g., by sample heating), which then act as a catalyst for the surface oxidation, appears possible. Future studies utilizing mini-cells with integrated thermocouples will have to clarify which one of the two scenarios holds true.

In summary, we have presented an experimental investigation of a sulfate formation at the water/CISSe interface. The findings demonstrate that there is a direct correlation between oxidation and sodium enrichment at the interface. The demonstrated general approach of utilizing X-ray emission spectroscopy to study chemical reactions in-situ can be extended to many other liquid-solid interfaces and also lends itself to the study of liquids and solutions as well.

REFERENCES

1. M. A. Green, K. Emery, D. L. King, S. Igari, and W. Warta, Solar Cell Efficiency Tables (Version 17); Progr. Photovolt. Res. Appl. **9**, 49 (2001).
2. C. Heske, U. Groh, O. Fuchs, E. Umbach, N. Franco, C. Bostedt, L.J. Terminello, R.C.C. Perera, K.H. Hallmeier, A. Preobrajenski, R. Szargan, S. Zweigart, W. Riedl, and F. Karg, phys.stat.sol. (a) **187**, 13 (2001).
3. L. Kronik, D. Cahen, and H.W. Schock, Adv. Materials **10**, 31 (1998).
4. C. Heske, G. Richter, Zhonghui Chen, R. Fink, E. Umbach, W. Riedl, and F. Karg, J. Appl. Phys. **82**, 2411 (1997).

This work was supported by the German ministries BMBF (FKZ 01SF007) and BMWI (FKZ 0329889, FKZ 0329218C), as well as the DFG through SFB 410, TP B3.

Principal investigator: Clemens Heske, Eberhard Umbach, Experimentelle Physik II, University of Würzburg, Germany. Email: heske@physik.uni-wuerzburg.de. Telephone: ++49-931-888-5127.