

Thin film solar cells: Damp heat-induced sulfur oxidation at the buried ZnO/Cu(In,Ga)(S,Se)₂ and ZnO/CdS/Cu(In,Ga)(S,Se)₂ interfaces

C. Heske¹, U. Groh¹, E. Umbach¹, S. Zweigart², and F. Karg³

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

² Siemens AG, ZT EN 2, D-81730 Munich, Germany

³ Siemens Solar GmbH, D-81739 Munich, Germany

INTRODUCTION

The long term stability under environmental conditions is one of the crucial factors for a commercial success of solar cells. In order to simulate and test the impact of real-life conditions such as humidity, heat, and variation in illumination intensity, solar cells are generally exposed to accelerated lifetime tests. One of these tests is called the "damp heat test": solar cells are exposed to a relative humidity of 85 % at 85 °C over a prolonged period of time in darkness.

Thin film solar cells based on Cu(In,Ga)(S,Se)₂ (CIGSSe) have reached a very high level of sophistication in terms of conversion efficiency (up to 18.8 % [1]), and, with appropriate encapsulation, CIGSSe cells have been able to pass the damp heat test [2]. However, such encapsulation is highly undesirable, and hence there is no alternative to the attempt of understanding the impact of damp heat tests on the electronic and chemical properties of *unencapsulated* solar cell devices. This understanding, however, is still in its infancy. First experiments [3] with unencapsulated cells indicate that there is a significant loss in the fill factor (about 20 %) and in the open circuit voltage (about 5 %) after an exposure of 100 h. These effects are thought to be correlated with (a) a change at the absorber/buffer interface (i.e., the CdS/CIGSSe interface) and/or the window layer (i.e., the ZnO/CdS layer) and (b) an increase of the defect density in the CIGSSe absorber. Since X-ray emission spectroscopy (XES) is an ideal technique to study the chemical properties at buried interfaces, we have hence performed an XES investigation of ZnO/CIGSSe and ZnO/CdS/CIGSSe thin film solar cells with and without damp heat treatment in order to study the chemical effects of such treatments in detail.

EXPERIMENT

XES experiments were carried out using the SXF endstation and the high flux capabilities of beamline 8.0. CIGSSe absorber films were prepared by rapid thermal annealing of elemental layers on Mo-coated soda-lime glass. In one sample series, the absorber was coated with a thin (20 nm) CdS film by chemical bath deposition. Then, both series were covered with a ZnO layer of varying thickness by sputter deposition. All samples were cut into two pieces, one of which was directly sealed under dry nitrogen atmosphere, while the other sample was subjected to a damp heat treatment (240 h, 85 °C, 85 % humidity) in darkness. After the damp heat treatment, the treated samples were also sealed under dry nitrogen atmosphere, and all samples were measured within the following week.

RESULTS AND DISCUSSION

To discuss the influence of the above described damp heat treatment on the buried interfaces, we start with the ZnO/CIGSSe material combination. While the ZnO/CdS/CIGSSe combination is currently the one with the highest reported conversion efficiency and represents the "standard" set-up, there is a strong drive for a replacement of the Cd-containing components. One such option is to deposit the ZnO directly onto the CIGSSe absorber. Furthermore, the effects to be discussed in this report are more clearly observed in the CdS-free system.

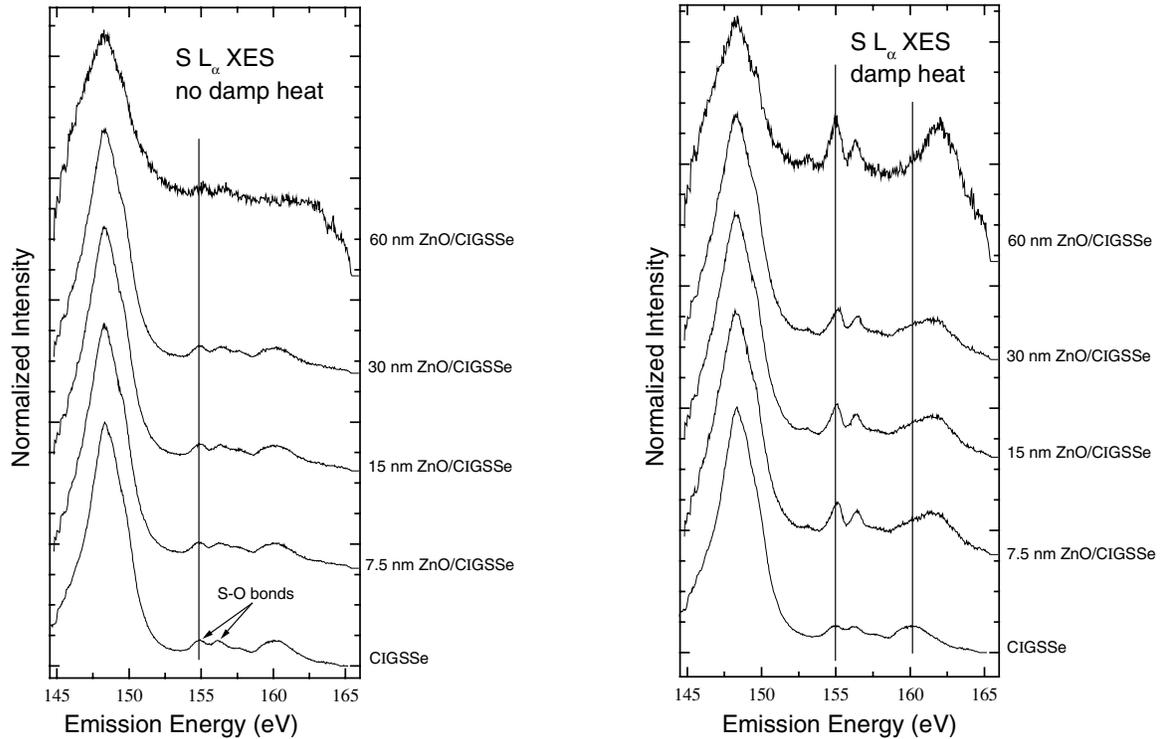


Figure 1. Sulfur L_{α} XES spectra of two ZnO/CIGSSe sample series with varying film thickness. The data on the left was obtained with samples from the standard preparation process, while the data on the right was taken after a damp heat treatment of each individual sample. All spectra are normalized to give equal emission intensity in the S 3s-related maximum around 148 eV.

Fig. 1 shows the S L_{α} XES spectra obtained for the ZnO/CIGSSe series. The left graph presents the data measured for standard samples (i.e., without damp heat treatment) for a variety of film thicknesses. The corresponding spectra for damp-heat treated samples are shown on the right. All spectra are normalized to the emission of the S 3s related electronic states around approx. 148 eV. As marked in the left graph, there are several spectral features pertaining to S-O bonds in addition to the expected spectral lineshape from S atoms in CIGSSe. Such a sulfur oxidation is not entirely surprising, because the sulfurization step and most of the sample handling is done under industrial (non-UHV) conditions. The intensity of these S-O features relative to the S 3s peak is not drastically changed upon deposition of ZnO (left graph). However, we observe a small change in the intensity of the S-O features as compared to the peak at 160 eV (associated with Cu-S bonds), indicating that the details of the oxygen-containing environment of emitting sulfur atoms may change during the ZnO deposition.

A much more pronounced effect is observed for the damp heat-treated samples: clearly, the intensity of the S-O features is strongly increased with respect to the S 3s emission line. We observe a small shift of the emission features around 156 eV and a more pronounced change in the spectral shape above 158 eV. The latter is interpreted as an occupancy of S-3d related states, hence pointing towards an increase in the amount of oxygen atoms bound to the emitting sulfur atom. The resulting spectrum for emission energies above 152 eV very closely resembles the spectrum typically observed for sulfate materials (such as $ZnSO_4$). We thus interpret the obtained results in such a way that the damp heat treatment enhances the formation of S-O bonds at the buried ZnO/CIGSSe interface.

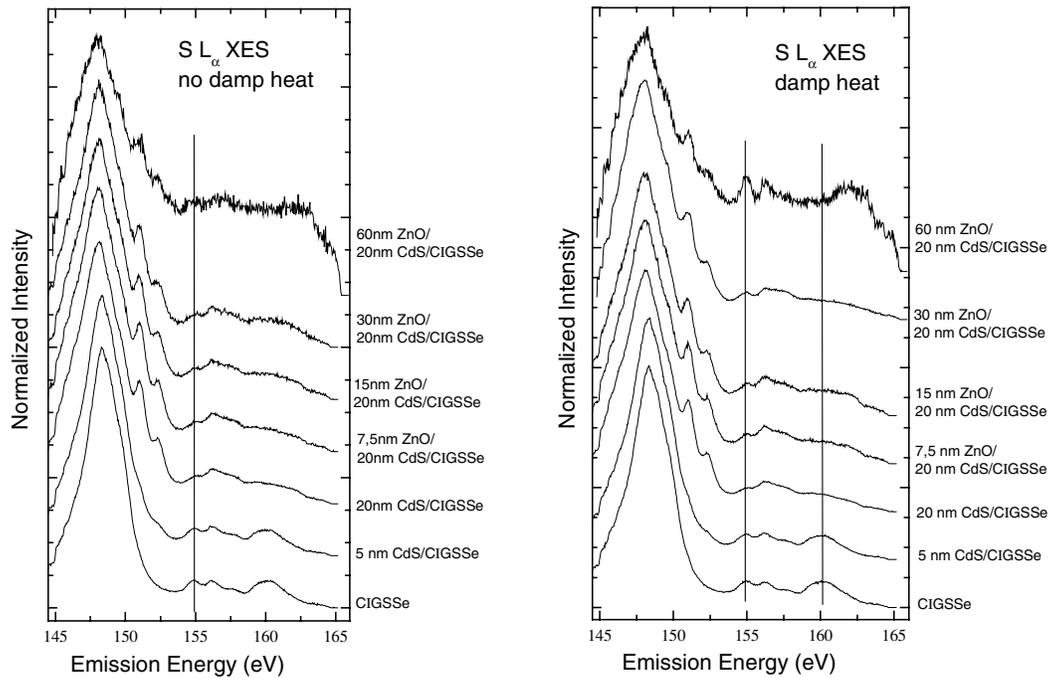


Figure 2. Sulfur L_{α} XES spectra of two ZnO/CdS/CIGSSe sample series with varying film thickness. Again, the data on the left was obtained with samples from the standard preparation process, while the data on the right was taken after a damp heat treatment of each individual sample.

Similar results are obtained for the ZnO/CdS/CIGSSe system (Fig. 2). Again, with respect to the S 3s emission, we find an increase of the S-O-peaks for the damp heat-treated samples which contain ZnO, while there is no significant increase for the untreated samples. This suggests an enhancement of the S-O bonding at the ZnO/CdS interface. Also, we again find a change in the intensities of the S-O peaks relative to the Cu-S peak, suggesting a different detailed structure of the environment around the emitting sulfur atom. Note that due to the additional CdS layer, the described effects are much smaller in these spectra because of an additional spectral contribution from the sulfur atoms in CdS, e.g., the Cd 4d-related emission peaks between 150 and 155 eV.

In summary, we have utilized X-ray emission spectroscopy as a unique tool to investigate the oxidation behavior of buried interfaces. A damp-heat induced oxidation of S atoms at ZnO/CdS and ZnO/CIGSSe interfaces suggests a chemical process which is expected to have a significant impact on the electrical performance of CIGS thin film solar cells.

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Principal investigator: Prof. E. Umbach, Experimentelle Physik II, Universität Würzburg, Am Hubland, D-97074 Würzburg. Email: umbach@physik.uni-wuerzburg.de, heske@physik.uni-wuerzburg.de. Tel. ++49-931-888-5755.