Title
Nondestructive depth-resolved spectroscopic investigation of the heavily intermixed In2S3/Cu(In,Ga)Se2 interface

Permalink
https://escholarship.org/uc/item/2qp5w7zv

Author
Bar, Marcus

Publication Date
2010-09-01

Peer reviewed
Nondestructive depth-resolved spectroscopic investigation of the heavily intermixed \( \text{In}_2\text{S}_3/\text{Cu(In,Ga)Se}_2 \) interface

M. Bär,1,2,3 N. Barreau,3,4 F. Couzinié-Devy,3 S. Pookpanratana,2 J. Klaer,1 M. Blum,2,4 Y. Zhang,2 W. Yang,5 J. D. Denlinger,5 H.-W. Schock,1 L. Weinhardt,4 J. Kessler,3 and C. Heske5

1 Solar Energy Research, Helmholtz-Zentrum Berlin für Materialien und Energie GmbH, Lise-Meitner-Campus, Hahn-Meitner-Platz 1, 14109 Berlin, Germany
2 Department of Chemistry, University of Nevada, Las Vegas (UNLV), Las Vegas, Nevada 89154-4003, USA
3 Institut des Matériaux Jean Rouxel (IMN)-UMR 6502, Université de Nantes, CNRS, 2 rue de la Houssinière, BP 3229, 44322 Nantes Cedex 3, France
4 Experimentelle Physik VII, Universität Würzburg, 97074 Würzburg, Germany
5 Advanced Light Source (ALS), Lawrence Berkeley National Laboratory, Berkeley, California 94720, USA

The chemical structure of the interface between a nominal \( \text{In}_2\text{S}_3 \) buffer and a \( \text{Cu(In,Ga)Se}_2 \) (CIGSe) thin-film solar cell absorber was investigated by soft x-ray photoelectron and emission spectroscopy. We find a heavily intermixed, complex interface structure, in which Cu diffuses into (and Na through) the buffer layer, while the CIGSe absorber surface/interface region is partially sulfurized. Based on our spectroscopic analysis, a comprehensive picture of the chemical interface structure is proposed.

\( \text{Cu(In,Ga)Se}_2 \) (CIGSe) thin-film solar cells with an n\( ^+ \)-ZnO/i-ZnO/CdS/CIGSe/Mo/glass device structure have reached efficiencies of 20%.\(^5\) To replace the CdS layer by a nontoxic, more transparent buffer, and the conventionally used chemical bath deposition by a technique allowing in-line processing, \( \text{In}_2\text{S}_3 \) layers have been deposited by physical vapor deposition,\(^2\) sputtering,\(^3\) atomic layer deposition,\(^4\) and spray ion layer gas reaction.\(^5\)

The \( \text{In}_2\text{S}_3/\text{CIGSe} \) interface has been previously investigated by different destructive depth-profiling techniques,\(^2,6\) high-resolution transmission electron microscopy and energy dispersive x-ray analysis,\(^7,8\) and x-ray photoelectron spectroscopy (XPS).\(^9\) At (post-)deposition annealing temperatures necessary for high device efficiencies (200–250 °C), a pronounced diffusion of Cu and Na from the CIGSe/Mo/glass substrate into the nominal \( \text{In}_2\text{S}_3 \) buffer layer was found in these studies. However, a complete picture of the chemical interface structure is still missing. In this paper, we will report on the characterization of the \( \text{In}_2\text{S}_3/\text{CIGSe} \) interface by a combination of nondestructive techniques [XPS and soft x-ray emission spectroscopy (XES)], deliberately varying the probing depth. Our measurements result in a depth-resolved picture of the interface in unprecedented detail.

\( \text{In}_2\text{S}_3/\text{CIGSe} \) structures were prepared at IMN on Mo/glass substrates.\(^10\) The absorber layers were dipped in NH\(_3\) solution (1 M, room temperature, 1 min) prior to the \( \text{In}_2\text{S}_3 \) buffer layer deposition by thermal coevaporation of elemental indium and sulfur at 200 °C substrate temperature. To vary the \( \text{In}_2\text{S}_3 \) thickness, different deposition times were used. The standard 80 nm buffer used in solar cells is prepared in 10 min (called “1/1” in the following). For reference, an \( \text{In}_2\text{S}_3 \) layer, different \( \text{In}_2\text{S}_3/\text{Cu} \) standards, and a CuInS\(_2\) (CIS) absorber\(^11\) were deposited on Mo/glass substrates. After preparation, all samples were sealed in polyethylene bags filled with dry N\(_2\) and desiccant for transport. At UNLV the samples were transferred into the analysis chamber (base pressure <5 × 10\(^{-10}\) mbar) without air exposure. XPS was performed using Mg K\(_\alpha\) and Al K\(_\alpha\) excitation and a Specs PHOIBOS 150 MCD electron analyzer (calibrated according to Ref.\(^12\)). Subsequently, XES was performed at the ALS using the soft x-ray fluorescence endstation of Beamline 8.0.

XPS survey spectra (not shown) show all expected absorber photoemission lines, Na-related peaks, and only minor spectral contributions of C- and O-containing surface contaminants. The former is due to the well-known diffusion of Na from the soda-lime glass substrate through the Mo and CIGSe layers,\(^13\) the latter indicates an IMN-to-UNLV sample transfer with minimal sample contamination. Upon \( \text{In}_2\text{S}_3 \) deposition, S-related peaks can also be observed. Furthermore, the intensity of all absorber-related lines (except In) decreases. However, we find significant differences in the attenuation behavior of the different CIGSe-related peaks. We have thus quantified the corresponding photoemission lines by a simultaneous fit of the spectra of all samples, using Voigt profiles and a linear background. For spin-orbit doublets, the respective, Gaussian and Lorentzian widths were coupled for each component and for all samples, and the intensity ratio was fixed according to the (2j+1) multiplicity. Figure 1(a) shows the intensity evolution of the different photoemission lines upon \( \text{In}_2\text{S}_3 \) deposition, normalized to the corresponding peak intensities of the bare (i.e., uncovered but NH\(_3\)-etched) CIGSe absorber and the 1/1-\( \text{In}_2\text{S}_3/\text{CIGSe} \) sample, respectively. As expected, the intensities of the S- and In-related lines increase, while those of the Ga- and Se-related peaks decrease. In accordance with the diffusion found in Refs.\(^4\) and 7–9, the Cu signal only decreases to approximately 40% of its initial intensity. The Na 1s intensity first increases and then decreases again to the same level as for the bare CIGSe surface. While the attenuation of the Se- and Ga-related peaks indicates a complete coverage of the absorber, the significant intensities for the Cu and Na signals point to a heavily intermixed interface between the \( \text{In}_2\text{S}_3 \) buffer and the absorber, in agreement with earlier
We observe that the Ga 2p signal is surprising, since the inelastic mean free path of the corresponding Se 3d photoelectrons (~2.5 nm in pure In2S3 using Mg Kα excitation) is significantly higher than that of the Ga 2p photoelectrons (~0.5 nm). We have computed the corresponding effective In2S3 thickness (d), assuming homogeneous and conformal absorber coverage, using I = I_0 \times \exp(-d/\lambda), where I (I_0) is the (un)attenuated signal intensity. Figure 1(b) shows the different effective thicknesses based on the attenuation of the Ga- and Se-related peaks (average of the Mg and Al Kα XPS measurements) in comparison with the nominal thickness. We observe that the Ga 2p-based effective thickness is (within the error bars) in good agreement with the nominal thickness, while the Se 3d- and Se 3s-based effective thicknesses are significantly increased. Only for the thinnest overlayer sample with observable Se signal (the 1/4 sample) do we observe an agreement with the nominal thickness. This finding could be due to a partial substitution of Se by S at the absorber surface, combined with a subsequent selenium sublimation (favored by the high selenium vapor pressure) in the first stages of In2S3 deposition. Although Se depletion of CIGSe surfaces due to vacuum annealing has not been reported for temperatures below 600 °C, temperatures in the range of the used substrate temperature for our In2S3 deposition are applied to re-evaporate Se caps from CIGSe. Furthermore, similar S/Se substitution processes have been observed upon CIGSe exposure to H2S atmosphere at high temperatures and after low-temperature chemical bath deposition of CdS.

Note that the calculated layer thicknesses for the 1/64- and 1/32-In2S3/CIGSe samples are—within the error bars—identical. Hence, we are using the computed thickness for thin In2S3 (instead of the nominal buffer thickness) as the comparative parameter for the following considerations.

To quantitatively assess the XPS data, the respective peak intensities were first corrected for the corresponding λ (Ref. 14) and photoionization cross section, as well as by the electron analyzer transmission. We find that both the Cu/Na and In/Na [S/Na] ratios measured with Al Kα are (47 ± 2)% [(16 ± 1)%] higher than those in the more surface-sensitive Mg Kα experiments. Our findings thus point to an accumulation of Na at all sample surfaces. The smaller Al Kα/Mg Kα difference for the S/Na ratio might indicate that also comparatively more S is present at the sample surface. We tentatively explain this with a formation of S–Na bonds at the In2S3/CIGSe sample surface. However, the presence of Na in the buffer bulk can also not be excluded.

The surface composition based on the XPS signal intensities is shown in Fig. 1(c) as a function of In2S3 thickness. Note that the S content was corrected to account for a possible Na2S formation at the surface: S = [S] – 1/2 × [Na]. For In2S3 thicknesses above 5 nm, the Cu:In:S composition is constant and in good agreement with a 1:5:8 stoichiometry, as indicated. This suggests a homogeneous buffer layer composition, independent of buffer layer thickness. For verification purposes, the determined In:S composition ([39:61]%) of an In2S3 reference layer is also shown.

To enhance bulk-sensitivity, we additionally characterized the In2S3/CIGSe samples with the more bulk-sensitive XES. Selected S L2,3 XES spectra are shown in Fig. 2(a). The spectrum of the bare (S-free) CIGSe absorber is ascribed to the significantly less intense Se M2,3 emission (note the magnification factor of x10). In contrast, the S L2,3 emission dominates the spectra even for the thinnest In2S3 layer. Apart from the expected increase in intensity with In2S3
thickness, the S L_{2,3} spectra of all In_{2}S_{3}/CIGSe samples look very similar at first glance. A closer look at the valence band features\(^ {20}\) between 153 and 163 eV in Fig. 2(b), however, reveals significant differences between the samples. The comparison with corresponding reference spectra shows that the S L_{2,3} spectra for thin In_{2}S_{3} layers are similar to that of the CIS reference, while the S L_{2,3} spectrum of the thick In_{2}S_{3}/CIGSe samples resembles that of the In_{2}S_{3}:Cu standards quite well.

To quantify the XES data, we used a sum of the CIS and In_{2}S_{3} reference spectra to (least-square) fit the valence band region, as exemplarily shown for the 10 nm In_{2}S_{3}/CIGSe sample in Fig. 2(c). The resulting spectral CIS and In_{2}S_{3} fractions are shown in Fig. 1(d). The CIS fraction is decreasing and the In_{2}S_{3} fraction is increasing with In_{2}S_{3} layer thickness. The quantified values confirm that the thick In_{2}S_{3}/CIGSe sample is very similar to the In_{2}S_{3}:Cu (18%) standard.

Assuming that the reference spectra represent stoichiometric CIS and In_{2}S_{3} samples and that the S L_{2,3} spectra of the In_{2}S_{3}/CIGSe samples can exclusively be represented as the superposition of the reference spectra, we compute a [Cu]/[In] ratio from the CIS and In_{2}S_{3} fractions: \([\text{Cu}]/[\text{In}] = 1/2 * S L_{2,3}(\text{CIS})/[1/2 * S L_{2,3}(\text{CIS}) + 2/3 * S L_{2,3}(\text{In}_{2}\text{S}_{3})]\). This ratio, which by design only takes into account Cu and In atoms bound to S, is shown in Fig. 1(e), together with the XPS-derived (total) [Cu]/[In] ratio. For the In_{2}S_{3}:Cu standards, the [Cu]/[In] ratios measured by energy dispersive x-ray spectroscopy\(^ {21}\) (EDS) are also shown and agree very well with the XES-based ratios. For the In_{2}S_{3}/CIGSe samples, we find similar XPS and XES [Cu]/[In] ratios for the thinnest and thickest but not the intermediate In_{2}S_{3} layers. The expected similar values for the thick samples are in agreement with a homogeneous CuIn_{2}S_{3} composition throughout the entire buffer. Since S L_{2,3} XES spectra only probe the chemical environment of the S atoms, only the S-containing CuIn_{5}S_{8} compound is considered.

The scheme in Fig. 2(d) summarizes the findings of our XPS and XES investigation. We suggest that, during In_{2}S_{3} coevaporation on a CIGSe substrate, a CuIn_{2}S_{8} buffer is formed, the absorber surface/interface region is chemically modified by a partial substitution of Se by S [probably resulting in a Cu(In,Ga)(S,Se)\(^ {2} \) interlayer], and Na and S accumulate at the sample surface, possibly forming Na_{x}S islands or a thin film. Acting as a Cu source for the CuIn_{2}S_{3} formation, the CIGSe absorber near the interface will be Cu-depleted. All of these chemical “modifications” are expected to have a significant impact on the electronic structure at the interface and thus on the overall solar cell performance.

The ALS is supported by the Department of Energy, Basic Energy Sciences, Contract No. DE-AC02-05CH11231.

---