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01/11/2007

Dear Bolko,

This is the second quarterly report of our second year in the Thin Film Partnership Program (Subcontract No. XXL-5-44205-12 to University of Nevada, Las Vegas: Characterization of the electronic and chemical structure at thin film solar cell interfaces). A brief summary and details of our activities are given below. This report is in fulfillment of the deliverable schedule of the subcontract statement of work (SOW).

Summary

This project is devoted to deriving the electronic structure of interfaces in $Cu(In,Ga)(S,Se)_2$ and CdTe thin film solar cells. By using a unique combination of spectroscopic methods (photoelectron spectroscopy, inverse photoemission, and X-ray absorption and emission) a comprehensive picture of the electronic (i.e., band alignment in the valence and conduction band) as well as chemical structure can be painted. The work focuses on (a) deriving the bench mark picture for world-record cells, (b) analyze state-of-the-art cells from industrial processes, and (c) aid in the troubleshooting of cells with substandard performance.

In the last months, we started to investigate CdS/CIGSe samples provided by the National Renewable Energy Laboratory (M. Contreras, R. Noufi), which currently holds the world record for respective solar cell devices in terms of photovoltaic performance. Thus, we aim for the bench mark picture of the chemical as well as electronic surface/interface structure of world record devices.

Detailed Description of the Activities:

In October 2006, we received a set of CdS/CIGSe samples from NREL. For those samples the CdS layer thickness was varied by means of taking the samples out of the chemical deposition bath after different times (0 - 16 min). See Table 1 for a complete list. All samples were characterized by X-Ray emission spectroscopy (XES) during our last experimental run at the Advanced Light Source (ALS) in October 2006. Fig. 1 shows the respective XES spectra of the Cd $M_{4,5}$ and In $M_{4,5}$ emission region on a linear (left) and logarithmic scale (right). Already after a deposition time of 1 min (and above), a Cd $M_{4,5}$ emission can be clearly identified (in particular on the logarithmic scale), which steadily

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Table I

Sample	CdS Deposition Time
C2106-11	0 min, bare absorber
C2106-21	1 min
C2106-12	2 min
C2106-22	4 min
C2106-18	8 min
C2106-23	16 min

increases with increasing deposition time. Consequently, the In $M_{4,5}$ emission intensity from the CIGSe substrate decreases due to the attenuation by the increasingly thick CdS layer. Close inspection of the data shows that the In $M_{4,5}$ emission is small, but still visible after a deposition time of 16 min. In order to quantify the thickness of the CdS layer using the XES data, we compared the CdS/CIGSe data with (reference) spectra of a thick CdS layer (not shown) and of the uncovered CIGSe substrate (bottom spectrum in Fig. 1). All measured spectra were described (in terms of a χ^2 fit) as a sum of the (weighted) reference CdS and substrate spectra:

$$sample = a \cdot CdS_{reference} + b \cdot substrate \quad (1)$$

To derive the thickness of the CBD-CdS layer deposited on CIGSe, we can use both, the

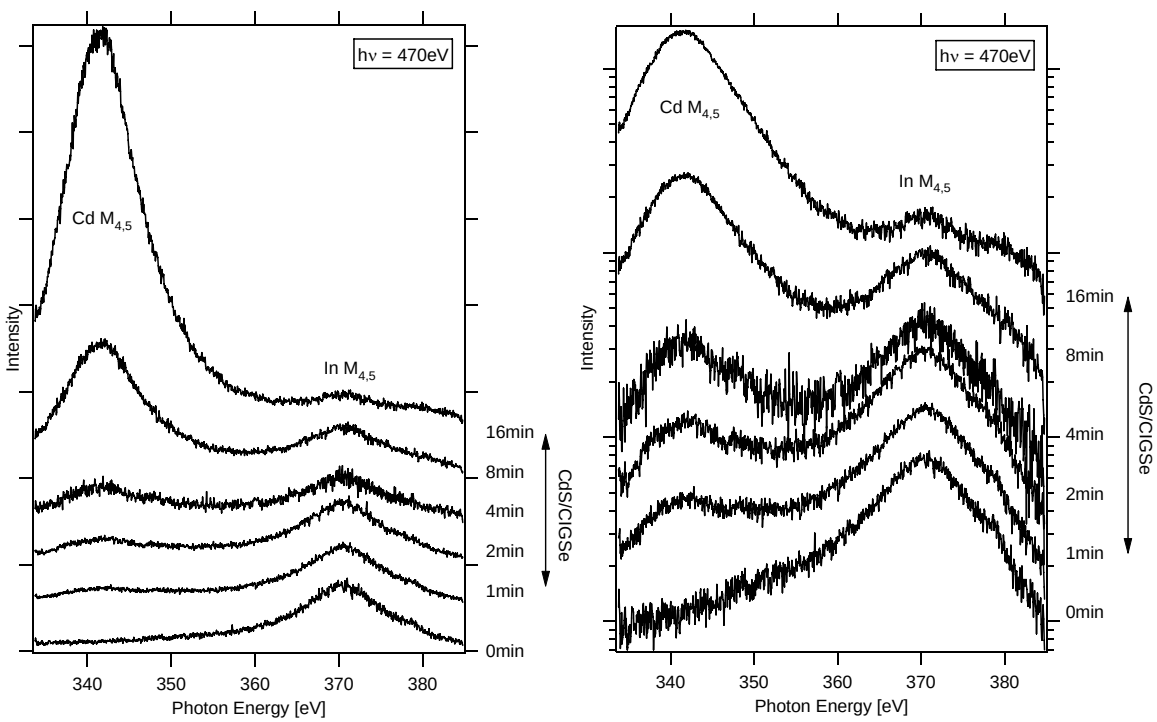

Fig. 1. *Cd $M_{4,5}$ and In $M_{4,5}$ X-ray emission spectroscopy of the investigated set of CdS/CIGSe samples on a linear (left) and logarithmic scale (right).*

attenuation of the In $M_{4,5}$ signal as well as the increase of the Cd $M_{4,5}$ intensity independently. If a homogeneous cover layer of thickness x attenuates the emission from the substrate, then the attenuated substrate emission intensity $I^{sub}(x)$ can be written as

$$I^{sub}(x) = I^{sub}_{ref} \cdot e^{-\frac{x}{\lambda^*}} \quad (2).$$

Similarly, the intensity of the emission from the cover layer $I^{cov}(x)$ can be written as

$$I^{cov}(x) = I^{cov}_{ref}\left(1 - e^{-\frac{x}{\lambda^*}}\right) \quad (3).$$

I^{sub}_{ref} and I^{cov}_{ref} denote the reference emission intensity of an uncovered substrate and of a cover layer of sufficient thickness, respectively ("sufficient" corresponds to a material thickness that results in a saturated emission intensity). Furthermore,

$$\frac{1}{\lambda^*} = \left(\frac{1}{\lambda_{exc} \cdot \sin\alpha}\right) + \left(\frac{1}{\lambda_{em} \cdot \sin\beta}\right) \quad (4),$$

where λ_{exc} and λ_{em} are the attenuation lengths in the cover layer for the excitation and emission energy, respectively. α and β are the angles of excitation and emission relative to the sample surface, respectively (in our case $\alpha = \beta = 45°$). In order to obtain the cover layer thickness x, we used the above-determined weighting factors a = $I^{cov}(x) : I^{cov}_{ref}$ and b = $I^{sub}(x) : I^{sub}_{ref}$ (see Eq. 1). The attenuation lengths associated with the Cd $M_{4,5}$ and In $M_{4,5}$ emission energies, the excitation energy, and the specific overlayer material (here: CdS) are listed in Table II. Assuming that the CdS layer homogeneously covers the substrate (as it can be expected if prepared by a wet-chemical deposition method such as CBD), the layer thicknesses on CIGSe were determined and are shown in Fig. 2 as a function of the deposition time. The given error is assumed to be dominated by the uncertainty in comparing absolute XES intensities due to sample (mis)alignment and is estimated to be 10% for the above-mentioned intensity ratios. For deposition times of 2 min and above, the

Table II

X-ray attenuation lengths in CdS (taken from [1]).

λ_{CdS} Cd $M_{4,5}$ emission (341.3 eV)	λ_{CdS} In $M_{4,5}$ emission (370.4 eV)	λ_{CdS} excitation (470.0 eV)
189 nm	216 nm	128 nm

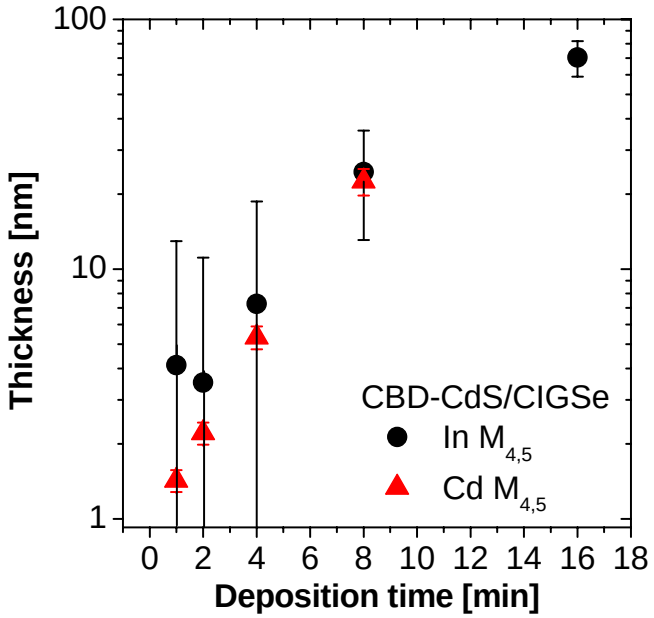

Fig. 2. *CdS layer thickness determined from the attenuation of the In $M_{4,5}$ emission of the substrate or from the increase of the Cd $M_{4,5}$ emission from the cover layer, respectively.*

values determined using the attenuation of the In $M_{4.5}$ CIS emission are (within the error bars) quite similar to those calculated from the increasing Cd $M_{4.5}$ cover layer emission intensity. Thus, both approaches (Eq. (2) and (3)) give consistent numbers. For thin cover layers the thickness determination based on the Cd $M_{4,5}$ emission intensity is more reliable as indicated by the smaller error bars. The thickness of the CBD-CdS layer after a deposition time of 16 min (which corresponds to the standard CdS buffer) on CIGSe is determined to be (70 ± 11) nm.

S $L_{2,3}$ spectra of the investigated set of samples and of a CdS reference were also recorded. They are shown in Fig. 3, again on a linear (left) and a logarithmic scale (right). The main peak of the CdS reference spectrum at 147.3 eV (which is actually a doublet indicated by the clearly visible shoulder at 149 eV) is due to S 3s electrons decaying into S $2p_{1/2}$ and S $2p_{3/2}$ core holes. In addition, the two peaks at 150.5 eV and 151.8 eV correspond to Cd 4d electrons decaying into the S $2p_{1/2}$ and S $2p_{3/2}$ core holes, respectively. They thus directly indicate sulfur atoms bound to Cd. Furthermore, we observe the upper valence band of CdS at about 156 eV. Comparing the spectra of the CdS/CIGSe samples with that of the CdS reference, it is obvious that they also show the typical features of a CdS S $L_{2,3}$ spectrum, especially when compared on logarithmic scale. As expected, this gets more distinct with increasing deposition time.

In an earlier paper [2], the absence of the features indicating S-Cd bonds was indicative of intermixing processes at the CdS/CIGSe interface. For a detailed evaluation of whether such effects also play a role here, the new spectra are shown in Fig. 4, left, with a normalization to their maximum. It can be observed that the spectrum of the bare (S-free!) CIGSe substrate shows different spectral features compared to the spectra of the S-containing samples. A magnified (smoothed) presentation of the CIGSe XES spectrum

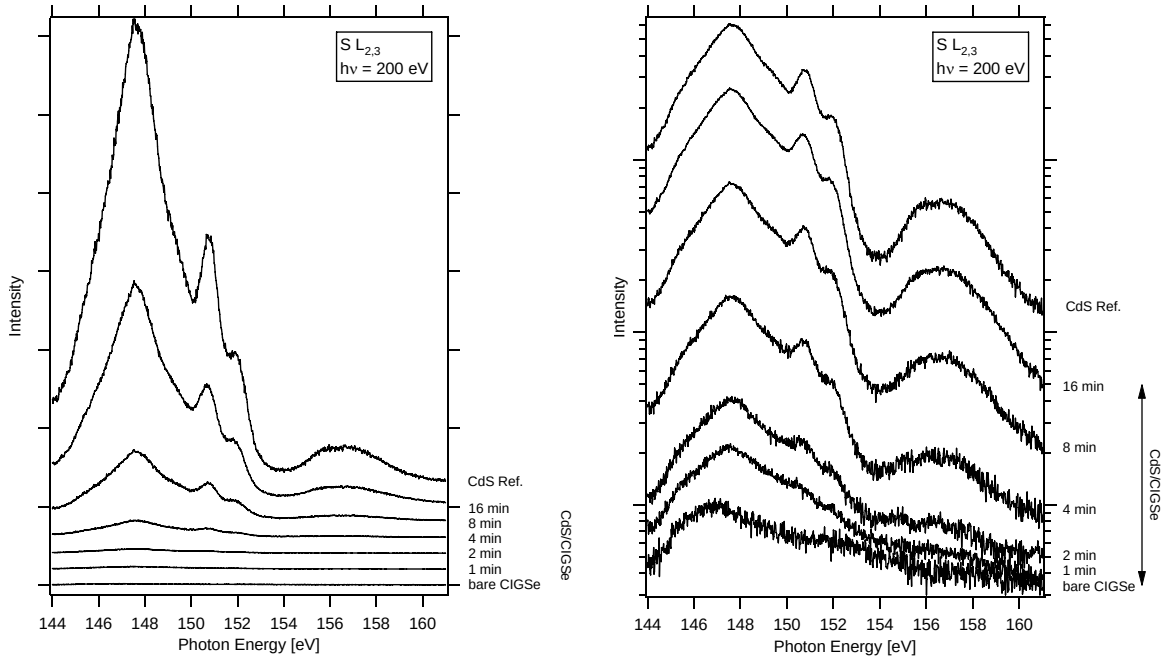

Fig. 3. *S $L_{2,3}$ emission of the investigated set of CdS/CIGSe samples on a linear (left) and logarithmic scale (right). For comparison also the spectrum of a CdS reference is shown*

shown in Fig. 4 (right) reveals two spectral features, which are separated by 5.7 eV. Since the latter agrees well with the doublet separation of Se $3p_{1/2}$ and Se $3p_{3/2}$, the features can most likely be attributed to Se 4s electrons decaying into Se $3p_{1/2}$ and Se $3p_{3/2}$ core holes. Note that our group has (for the last ten years) repeatedly searched for such Se 3p emission peaks; only recently, a significant improvement of the XES spectrometer has made it possible to observe such very weak structures.

A similar analysis approach as used above (i.e., describing the CdS/CIGSe spectra as a sum of the weighted reference CdS- and CIGSe-spectra) was used to clarify whether the intensity ratio between the features directly indicating S-Cd bonds and the main S 3s peak changes with deposition time or whether the spectra of the CdS/CIGSe samples can be explained by a (weighted) superposition of CdS and bare CIGSe reference spectra. The exemplary comparison of the experimental data of the “1 min” sample with a respective fit is shown in Fig. 5. The fit agrees quite well with the experimental data except between 150 -153 eV (the spectral range of the features directly indicating S-Cd bonds). We thus conclude that the spectra taken for thin CdS films can not be explained by a mere superposition of the Se substrate signal and the CdS reference. Nevertheless, in contrast to our earlier work, we find a clear Cd 4d signature (albeit smaller than for the CdS reference) even for the thinnest CdS film.

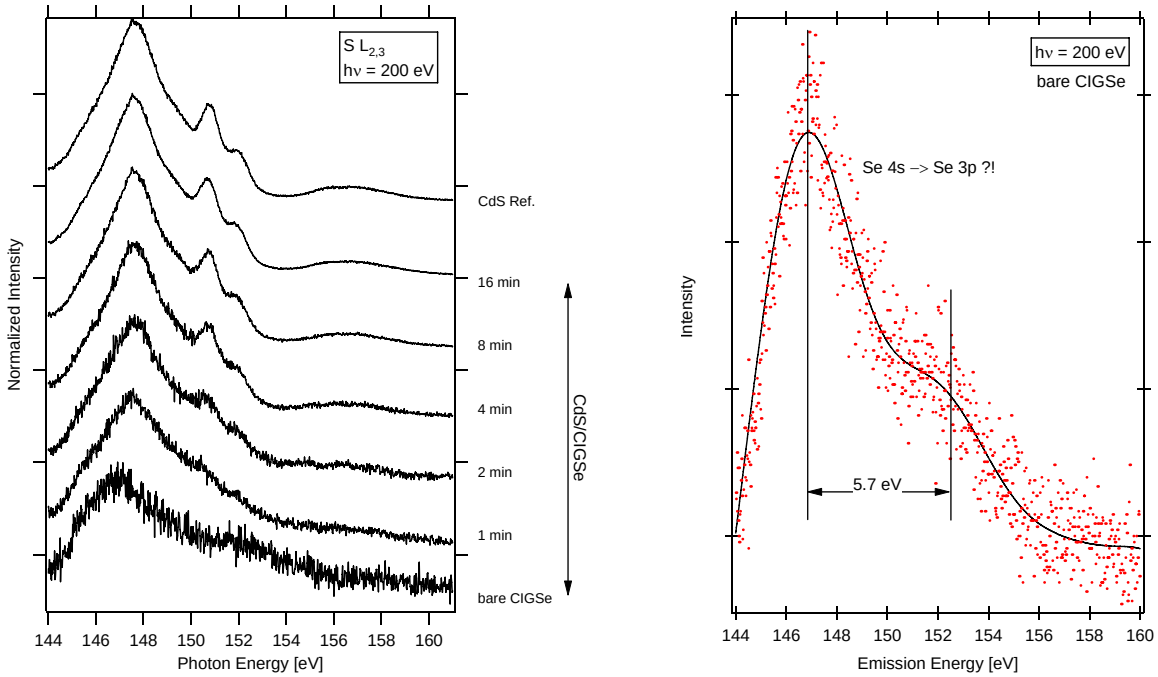

Fig. 4. *Normalized S $L_{2,3}$ emission of the investigated set of CdS/CIGSe samples (left). Magnified and smoothed presentation of the spectrum of the bare CIGSe sample (right): red dots: original data, black solid line: smoothed spectrum.*

This can be interpreted in the following way: We do not find any evidence for a very strong intermixing process (i.e., S atoms diffusing into the substrate). However, the

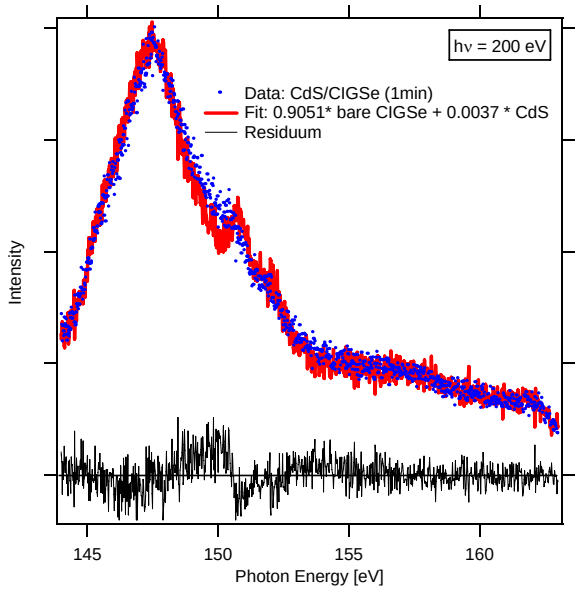

Fig. 5. *Comparison of the 'S $L_{2,3}$ spectrum' of the "1 min" CdS/CIGSe sample with a weighted superposition fit. In addition, also the residuum (difference between data and fit) is shown.*

environment of the sulfur atoms at the growth start of the interface clearly deviates from a perfect CdS environment. Whether this is due to a less perfect crystalline structure (i.e., the formation of very small nm-scale nanoparticles) or some S diffusing into the CIGSe absorber can not unambiguously be differentiated. We expect that surface-sensitive XPS experiments, which are currently being performed at UNLV, can shed more light on this question. Furthermore, the sample set is currently also being characterized by UV photo-electron and X-ray excited Auger electron spectroscopy as well as inverse photoemission in the lab at UNLV. The evaluation of this data with respect to determine the chemical as well as electronic structure of the CdS/CIGSe interface will be presented in a future report.

References:

[1] B.L. Henke et al., *Atomic Data and Nuclear Data Tables* **54**, 181 (1993); http://www-cxro.lbl.gov/optical_constants/atten2.html.

[2] C. Heske, D. Eich, R. Fink, E. Umbach,T. van Buuren, C. Bostedt, L. J. Terminello, S. Kakar, M. M. Grush, T. A. Callcott, F. J. Himpsel, D. L. Ederer, R. C. C. Perera, W. Riedl, and F. Karg, Appl. Phys. Lett. **74**, 1451 (1999).

If you have any questions, please do not hesitate to call me at (702) 895-2694.

Sincerely,

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CC: C. Lopez