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Dear Bolko,

This is the fourth report in Phase III of our Thin Film Partnership Program subcontract No. XXL-5-44205-12 (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 is painted. The work focuses on (a) deriving the bench mark picture for world-record cells, (b) analyzing state-of-the-art cells from industrial processes, and (c) aiding in the troubleshooting of cells with sub-standard performance.

Detailed Description of the Activities:

In February of 2008, the NREL group announced a new world record efficiency (19.9%) for $Cu(In,Ga)Se_2$ "CIGSe" – based thin-film solar cells [I. Repins et al., Prog. Photovolt. **16**, 235 (2008)]. This efficiency gain (compared to the former world record of 19.5%), is believed to be caused by a small – but apparently significant – change in the three-stage process, namely a termination of the third (and thus last) stage without Ga, hence leading to the formation of an "In-terminated" surface.

In our last quarterly report, we presented results of our x-ray photoelectron spectroscopy (XPS) investigation of the chemical structure of the topmost surface of respective samples. In this report, we focus on the complementary characterization of the surface-near bulk properties of the same samples by x-ray emission spectroscopy (XES). The latter analysis was conducted during our last experimental campaign at Beamline 8.0 of the Advanced Light Source, Lawrence Berkeley National Laboratory, in December 2008. In order to be able to directly compare the XES and XPS results, the identical samples were investigated, i.e., a $Cu(In,Ga)Se_2$ "CIGSe" sample from the world record absorber batch (M2992) and a CIGSe absorber (M2995) deliberately terminated with Ga for comparison.

As described in the last report, our XPS analysis showed that the change in the last deposition step of the three-stage process (the "In-termination") apparently results in a Cu-poorer *surface* composition of the world record M2992 sample compared to that of the Ga-terminated M2995 sample. We thus used XES in order to investigate whether this difference in the chemical structure is exclusively limited to the very surface of the samples (as probed by XPS) or whether the final termination during the absorber preparation also has an impact on the chemical structure of the sample bulk. Fig. 1 shows the respective spectra of the In $M_{4,5}$ and Cu $L_{2,3}$ emission (left) as well as Cu $L_{2,3}$ and Ga $L_{2,3}$ emission (right). The Cu $L_{2,3}$ levels appearing in the In $M_{4,5}$ emission window were excited by higher harmonics of the beamline and that the Cu $L_{2,3}$ emission in the In $M_{4,5}$ as well as both, the Cu $L_{2,3}$ and the Ga $L_{2,3}$ emission in the Ga $L_{2,3}$ emission window are detected in 2nd order of the spectrometer. All four spectra were normalized to the respective intensity maximum of the Cu $L_{2,3}$ XES peak. This allows a direct comparison of relative composition changes (in terms of the Cu:In:Ga ratio) in the surface-near bulk of samples M2992 (red spectra) and M2995 (black spectra). As can be observed in Fig. 1, the respective XES spectra agree very well between the investigated samples, indicating a very similar chemical structure. However, close inspection of the In $M_{4,5}$ emission in Fig. 1 (left) reveals that sample M2992 contains more In than M2995 and hence corroborates the more surface-sensitive XPS measurements,

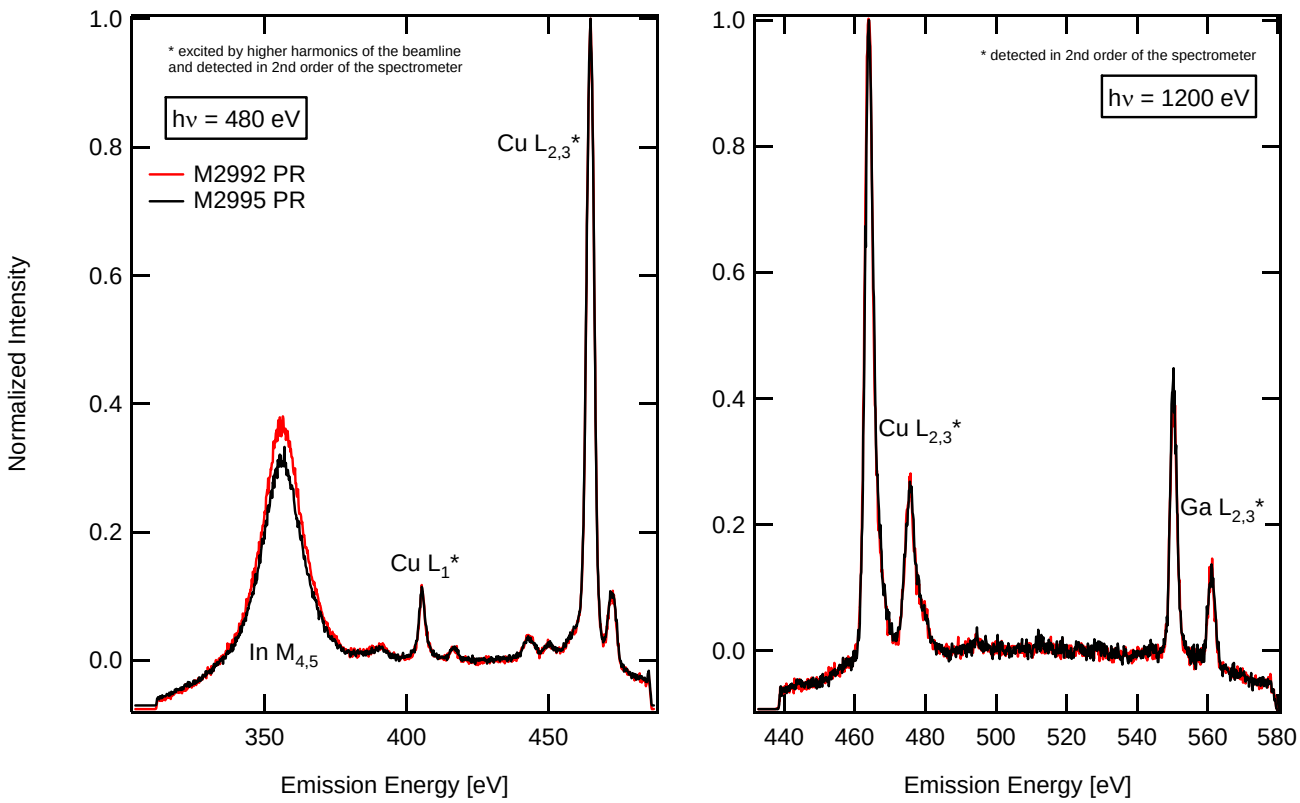

Fig. 1 *XES spectra (In $M_{4,5}$ and Cu $L_{2,3}$ [left] as well as Cu $L_{2,3}$ and Ga $L_{2,3}$ [right]) of the investigated CIGSe samples (M2992in red and M2995 in black). In both cases, the spectra were normalized to the maximum of the intensity of the Cu L_3 peak.*

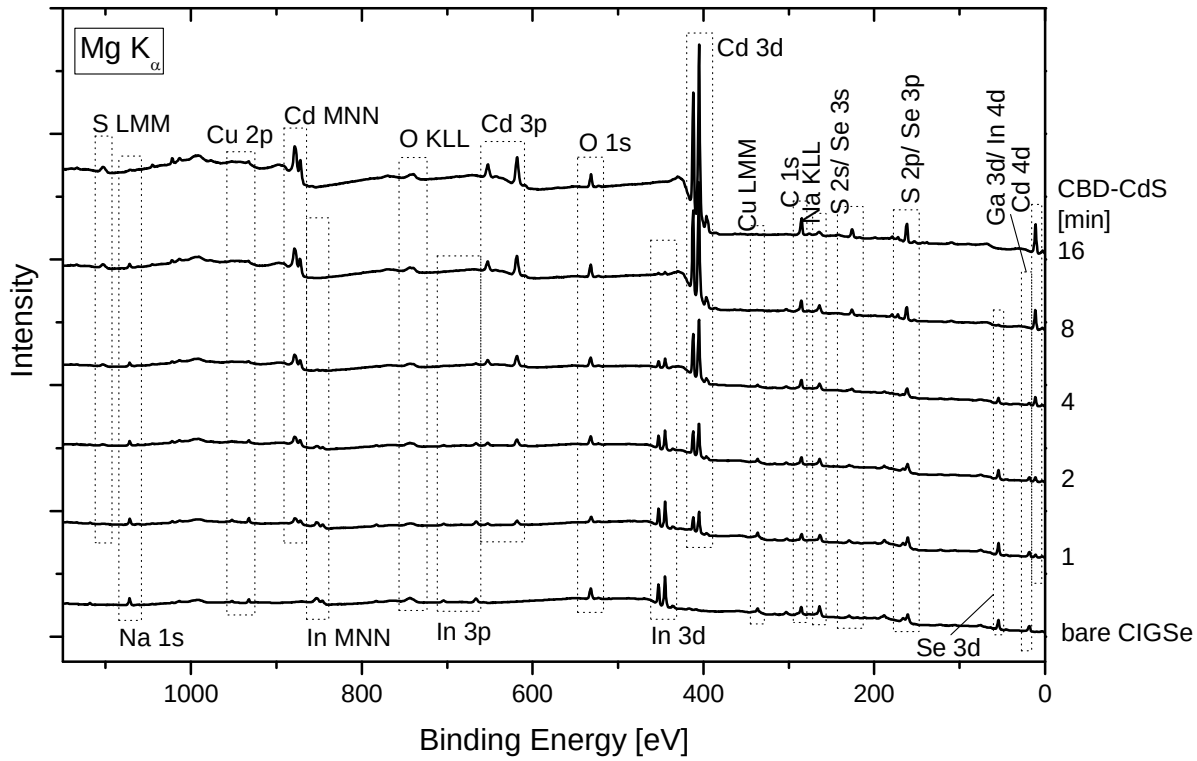

Fig. 2 *XPS survey spectra of a CdS/CIGSe deposition series.*

which revealed that M2992 is Cu-poorer (i.e., In-richer) at the surface than sample M2995. Since M2992 was In-terminated in the final phase of absorber preparation, the finding of more In is not that surprising. However, it is surprising that the effect of the In-termination can not only be observed in surface-sensitive XPS measurements but also in the here-presented surface-near bulk sensitive XES measurements, because the information depth of of XES is (in the considered energy range) around 150 nm, while the XPS information depth is on the order of a few nm.

A detailed analysis/modeling of the corresponding intensities combined with the respective information depths is currently being performed and will give quantitative information about the depth of this chemical modification of the absorber film. Furthermore, we are investigating the impact of the observed chemical modifications on the electronic surface and near-surface bulk structure, in particular the formation of the interface with CdS.

To that effect, we have initiated a detailed study of the CdS/CIGSe interface formation for world-record-class samples. A substantial data set has been recorded, and additional data-taking is currently ongoing. As an example, Fig. 2 shows a series of XPS survey spectra that were taken as a function of CdS thickness. Corresponding completed solar cell devices yielded efficiencies in the 15% range, while we are currently also investigating a sample series with efficiencies around 18%. These spectra, together with detail spectra of each core level, the valence band maxima, and the work function are currently being analyzed to develop a comprehensive picture of the electronic structure of these two CdS/CIGSe interface systems.

In the reporting period, the following manuscript was published:

“Depth-dependent band gap energies in $Cu(In,Ga)(S,Se)_2$ thin films“, M. Bär, L. Weinhardt, S. Pookpanratana, C. Heske, S. Nishiwaki, W. Shafarman, O. Fuchs, M. Blum, W. Yang, and J.D. Denlinger, Appl. Phys. Lett. **93**, 244103 (2008).

In the previous reporting period, the following manuscripts were published (but not listed in the last report):

"Chemical structures of the $Cu(In,Ga)Se_2$/Mo and $Cu(In,Ga)(S,Se)_2$/Mo interfaces", M. Bär, L. Weinhardt, C. Heske, S. Nishiwaki, and W. Shafarman, Phys. Rev. B **78**, 075404 (2008).

"Electronic level alignment at the deeply buried absorber/back contact interface in chalcopyrite-based thin film solar cells", M. Bär, L. Weinhardt, S. Pookpanratana, C. Heske, S. Nishiwaki, and W. Shafarman, Appl. Phys. Lett. **93**, 042110 (2008).

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

Sincerely,

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