Bolko von Roedern, MS 3212
National Center for Photovoltaics
National Renewable Energy Laboratory
1617 Cole Boulevard
Golden, CO 80401

09/15/2008

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 this year, the NREL group announced to have achieved a new world record efficiency (19.9%) for $Cu(In,Ga)Se_2$ "CIGSe" – based thin-film solar cells (Ingrid Repins, Miguel A. Contreras, Brian Egaas, Clay DeHart, John Scharf, Craig L. Perkins, Bobby To and Rommel Noufi, *19.9%-efficient ZnO/CdS/CuInGaSe_2 Solar Cell with 81.2% Fill Factor*, Prog. Photovolt. **16**, 235 (2008).) This recent efficiency gain (compared to the former world record - 19.5%), is believed to be caused by a small – but apparently significant – change in the three-stage process. In comparison to the deposition process used earlier, the difference resulting in the recent world record CIGSe absorber was a termination of the third (and thus last) stage without Ga and hence is considered to be "In-terminated".

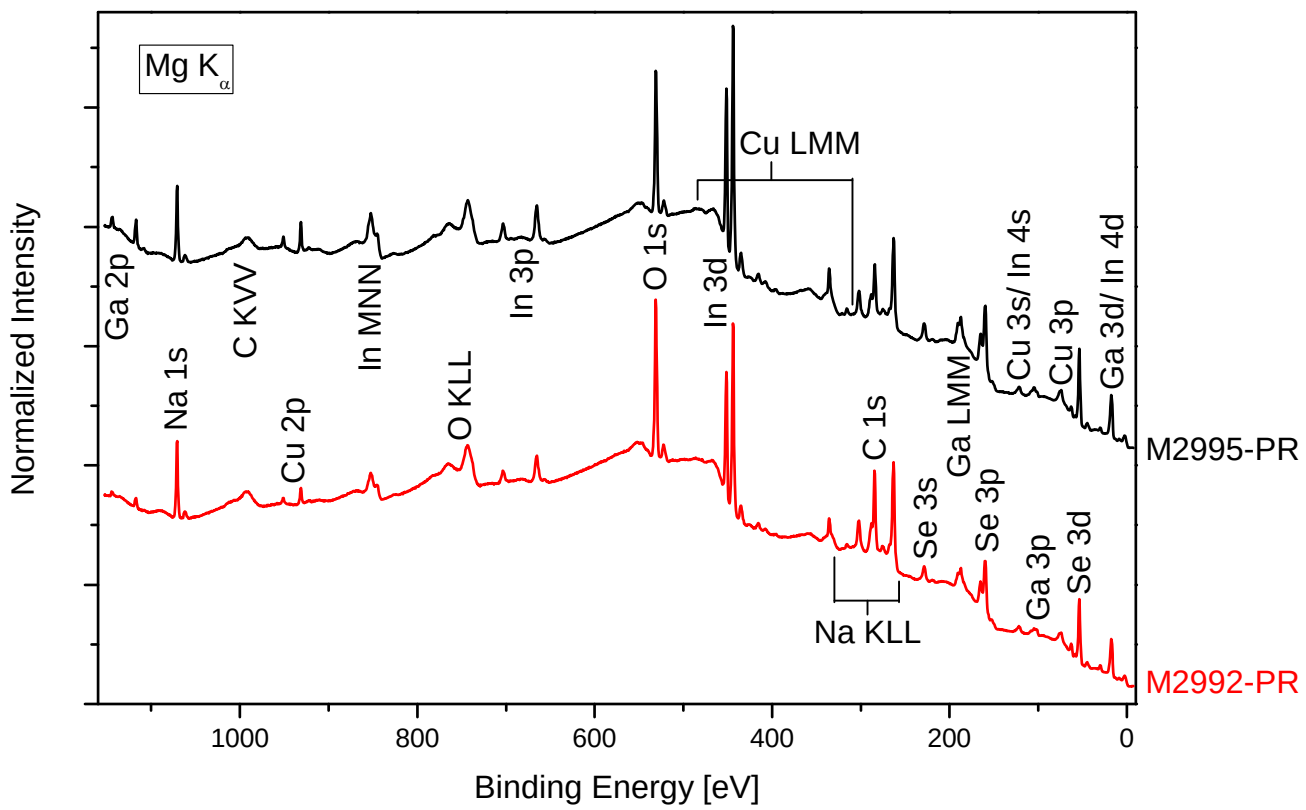

Fig. 1 *XPS survey spectra of the investigated CIGSe samples (as-received).*

In order to shed light on the expected different chemical surface structure, we investigated a sample from the world record absorber batch (M2992) by x-ray photoelectron spectroscopy (XPS) and x-ray excited Auger electron spectroscopy (XAES). Both techniques are very surface sensitive (information depth a few nm) and thus well suited to address questions of surface termination. In addition, we also characterized a CIGSe absorber (M2995) deliberately terminated with Ga for comparison.

Fig. 1 shows the XPS survey scans of the investigated CIGSe samples. As indicated by the high-intensity O-related XPS (O 1s) and XAES (O KLL) features, the surface of both samples is significantly oxidized. Corresponding detail spectra of photoemission and Auger features show that especially In and Ga are oxidized. The surfaces show also large amounts of Na and C. The C 1s photoemission line is composed of two pronounced contributions, of which the high-binding energy feature at approx. 289.6 eV is ascribed to carbonate. This interpretation also agrees with the line position of the O1s XPS peak. The position of the Na 1s photoemission line together with the modified Auger parameter of Na (Na 1s + Na KLL) furthermore suggests the formation of $NaCO_3$ at the sample surfaces. This pronounced sample surface contamination/oxidation can be explained by the extended storage of the samples in a desiccator and occasional exposure to air during different preceding characterization campaigns.

In the survey spectra in Fig. 1, we also observe a lower intensity of the Ga XPS and Auger features for the "In-terminated" sample (M2992) compared to the “Ga-terminated” sample (M2995). This

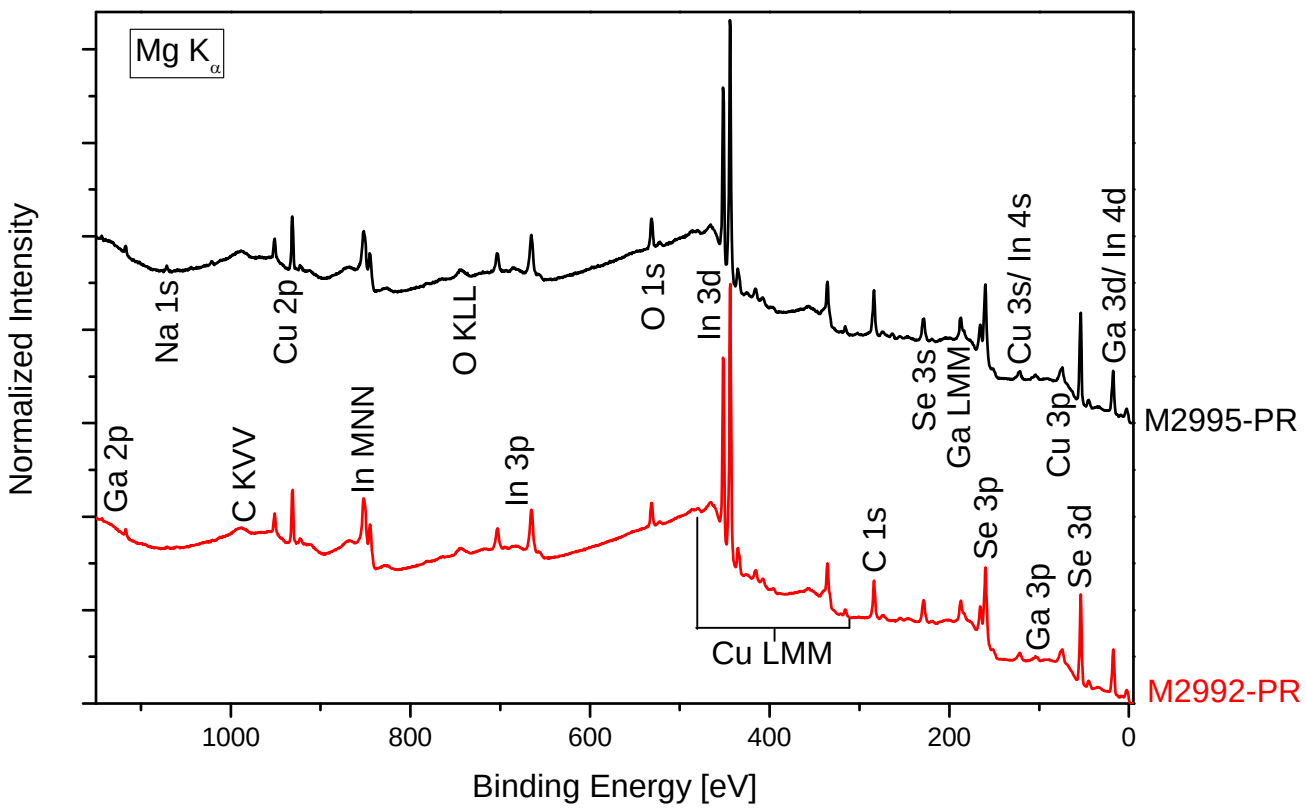

Fig. 2 *XPS survey spectra of the investigated CIGSe samples (after NH_3-dip).*

could indeed be the first indication for the expected different Ga/In surface ratio for the two samples. Note that, however, the higher degree of surface contamination for the "In-terminated" sample (as evident from the larger Na 1s, O 1s, and C 1s peaks) also leads to lower intensities of the corresponding In-related peaks. Since the emission of the Ga and In lines are governed by different attenuation lengths, a reliable quantitative analysis would required a detailed model of the nature, thickness, and morphology of the contamination layer, which is not avaible.

Usually, our group uses a mild (50 eV Ar+) ion treatment to clean the samples we are investigating. This ion energy is chosen since it is below the sputter threshold for chalcopyrites, leading primarily to ion-stimulated desorption of adsorbates and minimizing potential damage to the actual surface. In the present case, however, the surface contamination/oxidation was very pronounced, and thus we decided to clean the samples chemically by means of a short (2 min) dip in aqueous ammonia (at room temperature) performed in our N_2-filled glovebox. The corresponding XPS survey spectra are shown in Fig. 2.

Compared to the XPS survey spectra in Fig. 1, the spectra in Fig. 2 show that the intensity of the Na-, O-, and C-related features is significantly reduced. Correspondingly, the Cu and In photoemission and Auger feature detail spectra do not show any indications for the presence of oxides at the sample surface anymore. Hence, as expected, the NH_3 dip cleaned the surface of the investigated CIGSe samples (note that the residual oxygen signal is ascribed to residue from the aqueous solution dip).

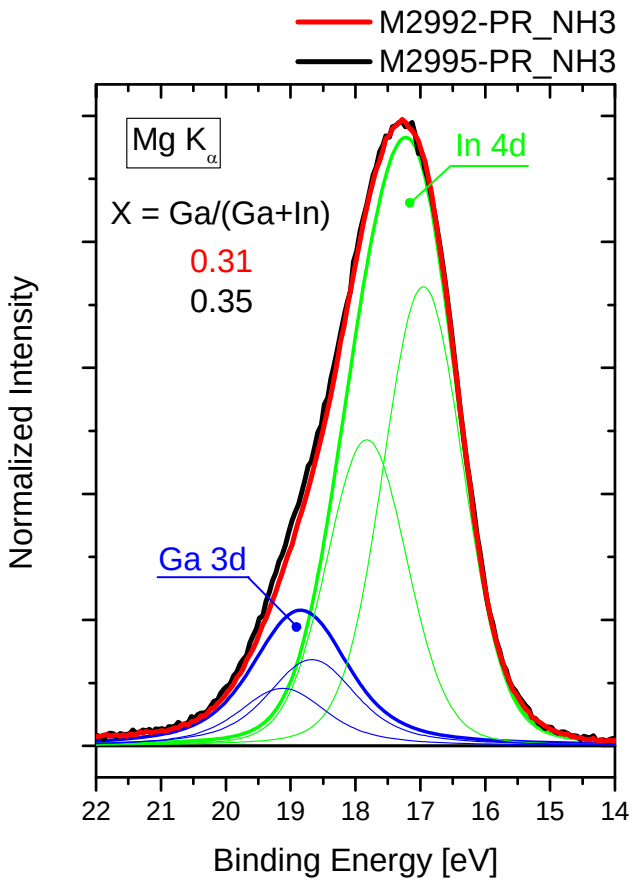

Fig. 3 *XPS detail spectra of the Ga 3d and In 4d photoemission lines of the investigated CIGSe samples (after NH_3-dip). Fit results (blue and green lines) are shown for the M2992 sample (red spectrum), and both spectra were normalized to maximum count rate.*

After the NH_3 dip, the survey spectra do not show a pronounced difference in the Ga/In ratio between the two samples. However, a detailed look at the Ga 3d and the In 4d photoemission line – shown in Fig. 3 – reveals that the Ga-terminated CIGSe surface has indeed a slightly higher Ga/(In + Ga) ratio compared to the world record "In-terminated" CIGSe sample.

An even more pronounced difference in the chemical surface structure of the CIGSe samples is revealed by the corresponding detail spectra of the valence band region (Fig. 4), which additionally suggests not only a difference in the Ga/In ratio but also in the overall stoichiometry at the surface. The overall Cu 3p intensity is constant, while both, the Se 3d and In 4d/Ga 3d intensities, are decreased. In terms of Cu : In : Se ratio, this suggests that the M-2992 sample surface is reduced in copper. Apparently, the change in the last deposition step of the three-stage process (the "In-termination") thus results in a Cu-poor surface composition of the world record M2292 sample (as found previously for highly-efficicent cells) compared to that of the Ga-terminated M2995 sample.

Hence, our next step is to investigate the impact of the observed differences in the chemical properties on the electronic surface structure by UV photoelectron spectroscopy and inverse photoemission,

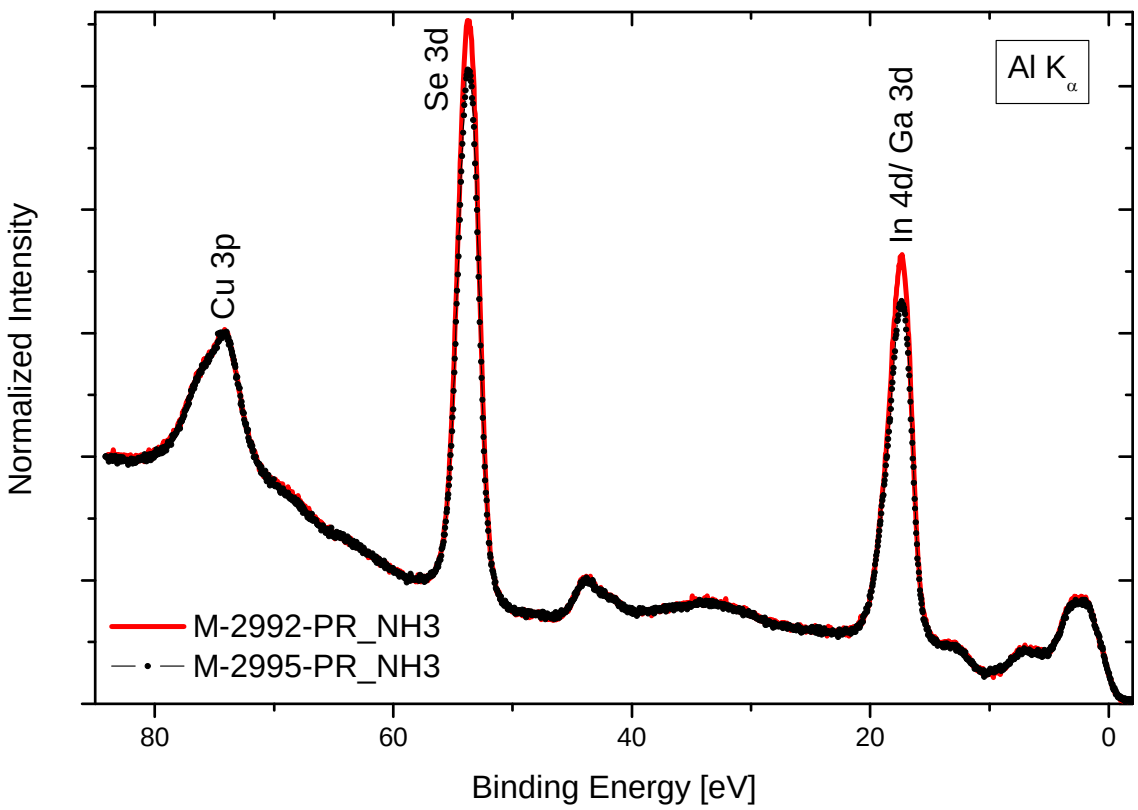

Fig. 4 *XPS detail spectra of the valence band region of the investigated CIGSe samples (after NH_3-dip). The spectra are normalized to equal measurement time and photon flux.*

which will give detailed information about the position of the valence and conduction band (and thus also the surface band gap), respectively.

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

Sincerely,

C. Heske
Associate Professor
Department of Chemistry
University of Nevada, Las Vegas

CC: C. Lopez

Department of Chemistry
4505 Maryland Parkway • Box 454003 • Las Vegas, Nevada 89154-4003
Tel (702) 895-2694 • FAX (702) 895-4072