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11/15/2007

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 have investigated the CdS/CIGSe interface at samples from NREL. By using a combination of x-ray photoelectron spectroscopy (XPS), ultra-violet photoelectron spectroscopy (UPS), and inverse photoelectron spectroscopy (IPES), we were able to directly determine the band alignment at this interface. We find a valence band offset of -0.90 (±0.15) eV and a flat conduction band alignment.

Detailed Description of the Activities:

In the past months we have continued the investigation of the CdS/CIGSe interface in samples prepared at NREL.

For the determination of the band alignment a series of CdS/CIGSe samples with different CdS thicknesses is needed. For the present study, in total six samples were prepared: a bare CIGSe absorber and five CBD CdS/CIGSe layers after different CdS deposition times (1, 2, 4, 8, and 16 min). To minimize surface contaminations, samples were packed under dry nitrogen in a sealed plastic bag with dessicant, shipped to UNLV, unpacked in

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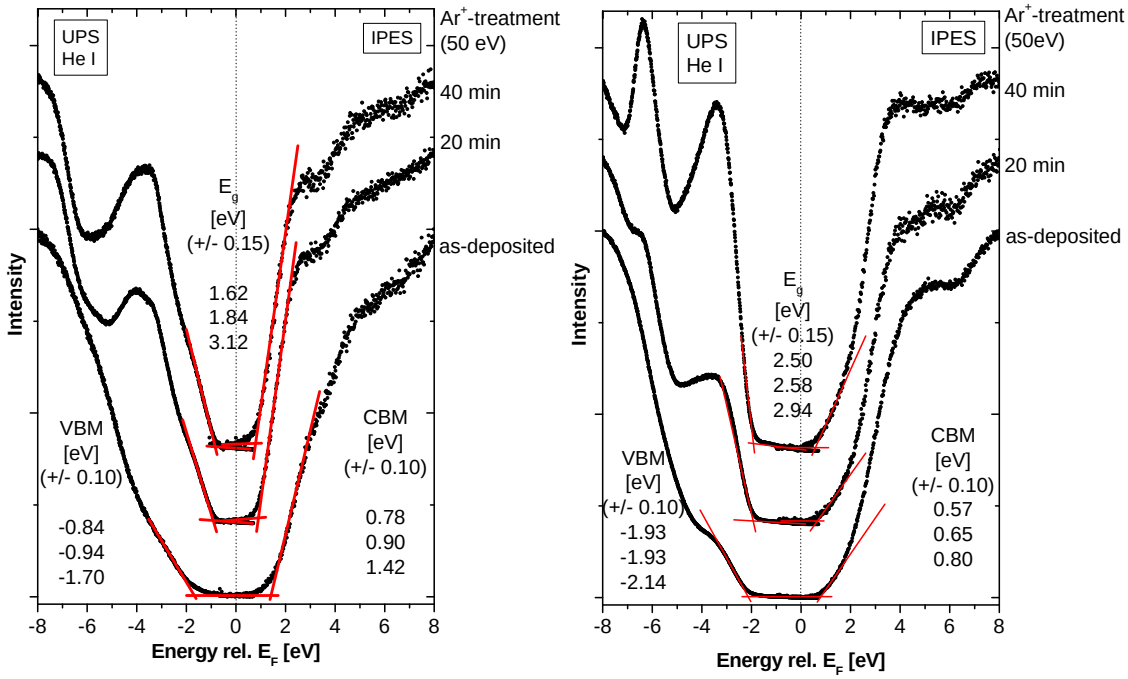

Fig. 1. *UPS and IPES spectra of absorber film (left) and the thick (16 min) CdS layer on CIGSe (right). To remove adsorbates from the surface both samples have been exposed to a mild Ar^+ ion treatment. The positions of the valence band maximum and conduction band minimum as derived by a linear extrapolation of the leading edges are given next to the spectra. The distance between valence band maximum and conduction band minimum gives the surface band gap, which is also listed.*

our glove-box under dry nitrogen, and then directly transferred into the ultra-high vacuum chamber for experiments.

For determining the band alignment at the interface, we have measured the valence and conduction band edges of the absorber film and the thick CdS film using UPS and IPES, as shown in Fig. 1. While samples were packed carefully, surface contaminations with C and O can not be entirely prevented. These surface contaminations obscure the determination of the band edges, clearly seen by the attenuated valence band signal related to Cu 3d electrons for the CIGSe absorber film (bottom left spectrum in the left panel of Fig. 1). Only after mild Ar^+ ion treatment of the surface (50 eV ions at a sample current of approx. 100 nA), we are able to remove these contaminations without structural damage to the absorber surface. After about 40 min of ion treatment, no further changes in the spectra are observed, and we can derive a surface band gap for the CIGSe absorber film of 1.63 (±0.15) eV. This band gap is increased with respect to the optical bulk value (1.23 eV), which can be explained by the copper-poor stoichiometry of the sample that we derive from our XPS measurements.
Similarly, the investigation of the CdS surface shows an increased surface band gap for the as-prepared surface. After cleaning with Ar^+ ions for 20 minutes the influence of the surface contaminations is largely removed, giving us a surface band gap of 2.50 (±0.15) eV, which agrees well with the (optically measured) bulk band gap of CdS.

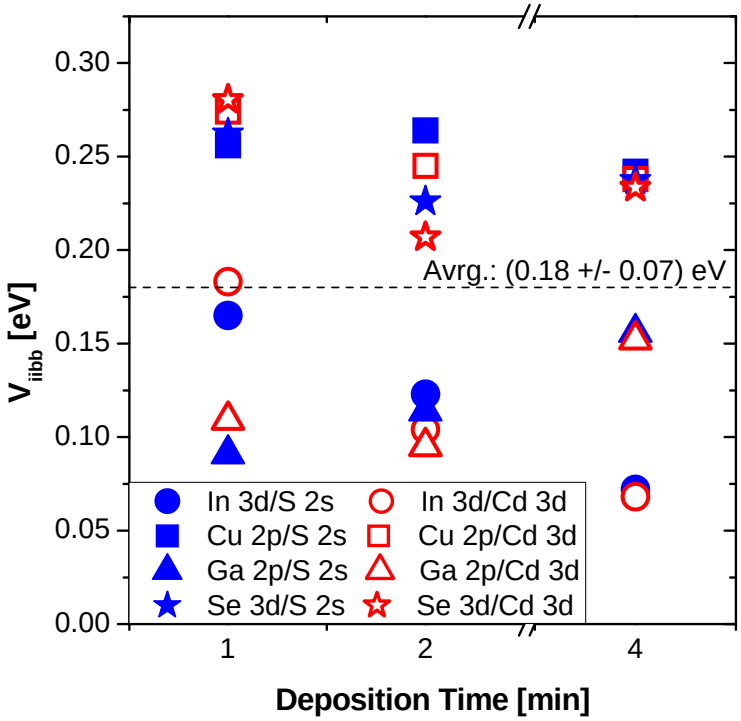

Fig. 2. *Values of the interface-induced band bending (iibb) as derived from monitoring the line shifts of different core levels.*

The band alignment at the CdS/CIGSe interface is now determined in two steps. In the first (approximate) step, we compare the band edge positions of the CIGSe absorber with those of the thick CdS/CIGSe film which are given in Fig. 1. This first approximation indicates a small cliff of 0.21 eV.

This value has now to be refined in the second step to account for changes in band bending of the absorber occurring when the interface to the CdS buffer layer is formed. This can be achieved by following the shifts of XPS core level positions of the absorber and the CdS buffer layer using the thin CdS/CIGSe samples (1, 2, and 4 min) where both lines from the CIGSe absorber and from the CdS buffer layer are visible. To minimize effects due to chemical shifts caused by bonding at the interface as well as possible intermixing of the layers, we have used different combinations of core levels of the CIGSe absorber and the CdS buffer layer as shown in Fig. 2. In total we have derived 24 different values and get a mean value of 0.18 (±0.07) eV. Compared to earlier investigations of this interface with different CIGSSe absorbers [1-3], this is the largest interface-induced band bending we have found, indicating the presence of an interface dipole. Furthermore, the overall spread of the various V_{iibb} values is smaller than that of other CdS/CIGSe interfaces for which significant S/Se intermixing at the interface could be shown [4] (note that, as reported previously [5], we did not find an indication for S/Se intermixing in the case of the NREL samples). These findings indicate a somewhat different chemical and electronic character of the CdS/CIGSe interface formation process at NREL compared to our previous work.

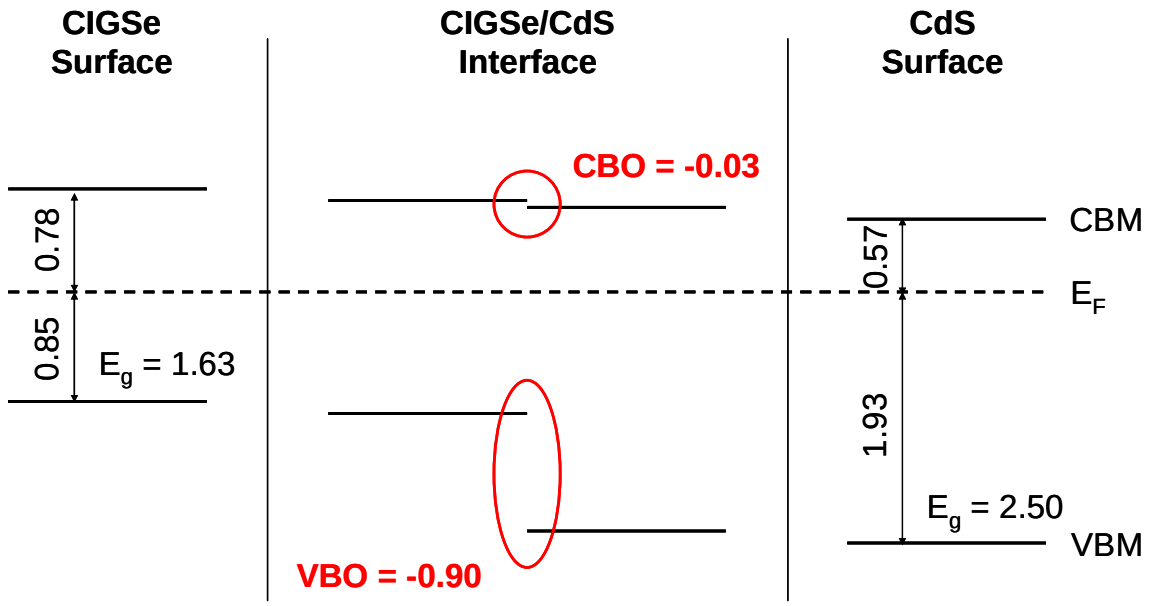

Fig. 3. *Schematic diagram of the band alignment at the CdS/CIGSe interface (all values are given in eV). The band extrema of the CIGSe and CdS surfaces (as determined by UPS and IPES) are shown on the left and right, respectively. The center shows the band alignment at the interface after taking the interface-induced band bending into account.*

We can now apply the correction for the interface-induced band bending to the conduction band minimum and valence band maximum values derived above to get the band alignment at the CdS/CIGSe interface. The results are shown in Fig. 3. We find a valence band offset of -0.90 (±0.15) eV and a flat conduction band alignment with an offset of -0.03 (±0.15) eV.

In summary, we have derived the electronic structure of the CdS/CIGSe interface in thin film solar cells prepared by NREL. The conduction band alignment at the CdS/CIGSe interface is flat, as expected for a high efficiency CIGSe solar cell. Furthermore, we find direct evidence for a strong interface dipole. Together with the previously reported lack of significant intermixing at the CdS/CIGSe interface, we thus find a modified electronic and chemical interface structure compared to previously studied (less efficient) devices from other manufacturers.

References:

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[2] "Band alignment at the CdS/$CuIn(S,Se)_2$ heterojunction in thin film solar cells", L. Weinhardt, M. Morkel, Th. Gleim, S. Zweigart, T.P. Niesen, F. Karg, C. Heske, and E. Umbach, Proc. 17th European Photovoltaic Solar Energy Conference, October 2001, Munich, p. 1261.

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Weinhardt, O. Fuchs, D. Groß, G. Storch, E. Umbach, N.G. Dhere, A.A. Kadam, S.S. Kulkarni, and C. Heske, Appl. Phys. Lett. **86**, 062108 (2005).

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[5] Annual report of this project, August 17, 2007.

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

Sincerely,

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