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Band lineup between CdS and ultra high vacuum-cleaved CuInS$_2$ single crystals

A. Klein,[a] T. Löher, Y. Tomm, C. Pettenkofer, and W. Jaegermann

Hahn-Meitner-Institut, Abteilung CG, Glienicker Strasse 100, 14109 Berlin, Germany

The interface formation between vacuum evaporated CdS and ultrahigh vacuum-cleaved CuInS$_2$ single crystals has been studied by synchrotron excited photoelectron spectroscopy. The valence band discontinuity is determined directly from valence band difference spectra to be ΔE_V =0.6 ($\pm$0.1) eV. This value is significantly smaller than for other preparation conditions given in the literature and evidently not suitable for solar cell applications. The similarity to observations at the CdS/CuInSe$_2$ interfaces suggests that neutrality levels play a dominant role in establishing the band lineup at interfaces containing chalcopyrite semiconductors. © *1997 American Institute of Physics.* [S0003-6951(97)01810-X]

Ternary chalcopyrite compounds CuInSe$_2$, CuGaSe$_2$, CuInS$_2$, and their quaternary alloys are intensively studied for potential thin film solar cell applications.[1] The highest solar cell efficiencies of about 17% for Cu(InGa)Se$_2$ have been obtained using chemically bath deposited CdS buffer layers. From environmental considerations it is suggested that one replace the Se in the absorber layer by sulfur. Efficiencies in excess of 10% have so far been obtained using ternary CuInS$_2$ layers.[2,3] The band discontinuities are crucial for high solar cell efficiencies. It is expected that best efficiencies using p-type absorbers are obtained for conduction band offsets close to zero.[4]

Photoelectron spectroscopy is widely used to determine valence band offsets of semiconductor heterojunctions. The valence band discontinuity ΔE_V for a semiconductor heterojunction can be determined from binding energy differences ΔE_{CL} of substrate and adsorbate core levels for coverages where both substrate and adsorbate emissions are present (5–30 Å).[5] This procedure requires the knowledge of core level binding energies with respect to the valence band maxima (BE_{VBM}) of either semiconductor. Positions of valence band maxima are determined by fitting experimentally broadened, theoretically calculated density of states to the leading edge of valence band emissions[6] or somewhat less accurate by its linear extrapolation.[7] This quantity is generally determined from bulk standards of the substrate and adsorbate (thick overlayer), respectively. The valence band discontinuity is then given by

$$\Delta E_V = (BE_{VBM}^s - BE_{VBM}^f) - \Delta E_{CL},$$

where s/f denote substrate/film, respectively. For nonreactive, lattice-matched semiconductor interfaces the photoelectron spectra are given as superpositions of undisturbed substrate and adsorbate emissions. If the valence band discontinuity is sufficiently high the valence band spectra clearly show the onset of both substrate and film valence emissions at intermediate coverages.[7] This offers the opportunity to directly determine the valence band offset from one single valence band spectrum, as demonstrated, e.g., by Löher et al. for the CdS/CuInSe$_2$ interface.[8]

The valence band discontinuity between chemically bath deposited CdS layers and KCN-etched CuInS$_2$ thin films has been determined by Hashimoto et al. as $\Delta E_V = 1.18$ eV (Ref. 9) and by Scheer et al. as $\Delta E_V = 1.5$ eV.[10] This experimental procedure tracks the preparation of thin film solar cells. However, the physical mechanisms which lead to the determined alignment of the bands remain almost unresolved because of the widely unknown atomic composition of the interface. Improved strategies for solar cell interface engineering would require a more detailed understanding of the underlying physics. The investigation of atomically clean and abrupt interfaces provides the starting point for an experimental separation of influences on band offsets of technologically prepared solar cell structures. From such kinds of studies it is now well established that the active interface in CdS/CuInSe$_2$ solar cells is not formed by direct contact of bulk CdS with bulk CuInSe$_2$.[8,11]

Photoelectron spectra in the course of CdS deposition on CuInS$_2$ are shown in Fig. 1. The spectra were recorded in normal emission with an angle resolving photoelectron spec-
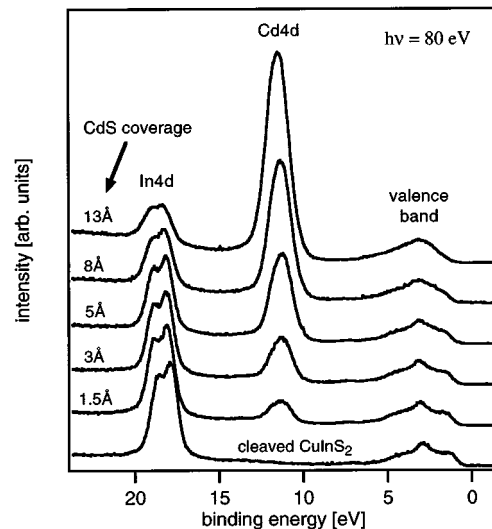

FIG. 1. Photoelectron spectra of In 4d-, Cd 4d-, and valence bands for CuInS$_2$ in the course of CdS deposition. Spectra are recorded with excitation energy $h\nu=80$ eV and normalized to the same valence band intensity for better visibility.

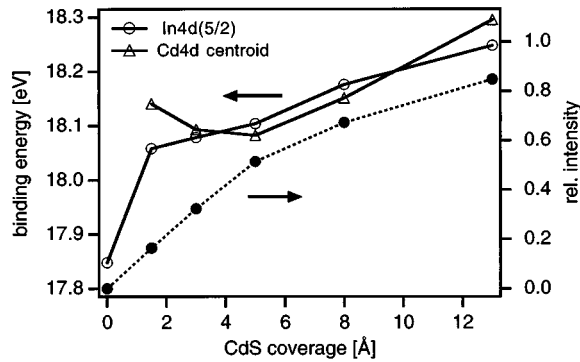
[a]Fax: ++49.30.80622434; electronic mail: klein@hmi.de

FIG. 2. Evolution of relative intensity (filled symbols) and binding energies (open symbols) of In $4d(5/2)$- and Cd $4d$ centroid positions in the course of CdS deposition. An offset of $+6.8$ eV is added to the Cd $4d$ binding energy value.

FIG. 3. Valence band difference between clean CuInS$_2$ and CuInS$_2$ covered with 8 Å CdS. The spectrum of the cleaved surface is shifted in binding by $+0.3$ eV and multiplied by 0.17, as adopted from evolution of In $4d$ core level.

trometer (VG ADES 500) attached to the TGM7 beamline of the BESSY storage ring in Berlin, Germany. As excitation energy $h\nu=80$ eV has been chosen which gives a combined resolution of monochromator and spectrometer of ≈ 0.5 eV. Binding energies are given with respect to the Fermi level of the metallic sample holder. The bottom most spectrum in Fig. 1 is taken from the uncovered surface immediately after cleaving in ultrahigh vacuum (UHV) ($p < 2 \times 10^{-10}$ mbar). From this spectrum we determined the binding energy of the In $4d(5/2)$ component to be 17.85 (± 0.01) eV. The energetic position of the valence band maximum has been determined to be $E_F - E_V = 0.65$ (± 0.03) eV. A Gaussian broadened line with a width of 0.5 eV has been fitted to the leading edge rather than using simple linear extrapolation. Hence we obtain a core level binding energy of $BE_{VBM}^{In\,4d(5/2)} = 17.2$ (± 0.03) eV. Hashimoto et al. give a value of 17.6 eV for the In4d centroid position with respect to the valence band maximum of their KCN-etched CuInS$_2$ film.[9] The centroid position should deviate from the In $4d(5/2)$ position by approximately half of the spin-orbit splitting of the In $4d$ level which amounts to 0.86 eV.[12] Therefore both values are in fairly good agreement.

CdS was deposited from a home made Knudsen cell with evaporation rate about 2.5 Å/min as determined using a water cooled quartz microbalance. During deposition the sample was kept at room temperature. The spectra in Fig. 1 are normalized to the same maximum valence band intensity for better visibility. With increasing CdS deposition, the In $4d$ emissions (BE ≈ 18 eV) become attenuated while the Cd $4d$ intensity (BE ≈ 11 eV) increases. Except for the last deposition step, the linewidths of In $4d$ and Cd $4d$ levels remain constant. The valence band features of CuInS$_2$ are gradually exchanged by structures characteristic for polycrystalline CdS.

Relative intensities and binding energy shifts are summarized in Fig. 2. The attenuation of substrate In $4d$ emissions with increasing coverage indicates two-dimensional growth mode. The binding energy difference between the In $4d(5/2)$ level and the Cd $4d$ centroid saturates at a value of $\Delta E_{CL} \sim 6.8$ eV after deposition of ~ 3 Å. Hashimoto et al.[9] give a binding energy difference between In $4d$ and Cd $4d$ centroids of $\Delta E_{CL} \approx 6.8$ eV. Corrected for the In $4d$
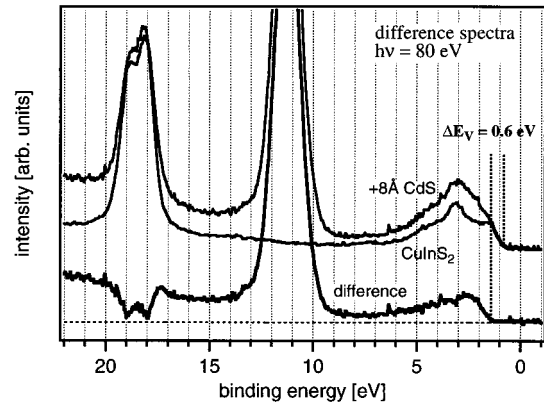
spin-orbit splitting this is about 0.4 eV lower than our value.

The determination of valence band offset is illustrated in Fig. 3. We performed difference spectra by subtracting the valence band measured for the uncovered surface from spectra obtained after deposition of 8 Å. For this purpose the spectrum of the uncovered surface is shifted in energy and reduced in intensity by values adopted from the evolution of the In $4d$ substrate line. The valence band difference shown at the bottom closely resembles the valence band spectrum obtained for the highest coverage (uppermost spectrum in Fig. 1), hence reflecting the contribution of CdS to the valence bands. The onset of emission is clearly identified in the difference spectra and is linearly extrapolated for the determination of the CdS valence band maximum. Since we know the position of the valence band maximum of CuInS$_2$ from the cleaved sample ($E_F - E_V = 0.65$ eV) its actual position is simply given by adding the induced band bending eV$_{bb}$, obtained from In $4d$ binding energy shifts. The valence band offsets obtained by this procedure are given by $\Delta E_V = 0.55$, 0.62, 0.63, and 0.61 eV for CdS coverages of 3, 5, 8, and 13 Å, respectively. For each value we estimated the experimental uncertainty to be less than 0.1 eV. Hence we find an average value of $\Delta E_V = 0.6$ (± 0.1) eV.

Using experimentally determined ΔE_{CL} and ΔE_V one may further evaluate the spectra with respect to the binding energy of the Cd $4d$. It is determined to be $BE_{VBM}^{Cd\,4d} = 9.8$ (± 0.1) eV, which is 0.2 eV larger than the value given by Hashimoto et al. for their chemically bath deposited CdS films.[9] This difference is most likely due to the different preparation of the CdS layer. It is known that chemically bath deposited CdS films contain oxygen in the order of 10% in the form of CdO or Cd(OH)$_2$.[13] The oxygen content may easily account for the shift of Cd $4d$ binding energy. However, it is also possible that different film preparation leads to differently strained overlayers which may also influence core level binding energies and valence band structure, at least for values of strain induced by the 5% lattice mismatch between CuInS$_2$ and cubic CdS.[14,15] Since we have deposited CdS on the sample kept at room temperature, we

would expect the film to grow in a polycrystalline mode with a large number of defects. Therefore our CdS should be fully relaxed already at very low coverages. This is also indicated by the coverage independent values of ΔE_{CL} and ΔE_V. Hence strain should not affect our determination of the Cd 4d binding energy.

The 0.4 eV difference in ΔE_{CL} values, which mainly accounts for the 0.6 eV difference in ΔE_V between this work and Ref. 9, may be due to different surface stoichiometry,[11] orientation[6] and/or adsorbed interlayers.[16] Clarification will need further investigation.

For vacuum deposited CdS on both cleaved chalcopyrite semiconductors CuInS$_2$ or CuInSe$_2$ (Ref. 8) a similar band diagram with approximately symmetric band alignment is observed. Experimental and theoretical studies of ZnSe/CuInSe$_2$ interfaces gave comparable results.[17] In all cases the band alignment seems to be governed by midgap charge neutrality levels in close agreement to heterointerfaces based on the related zincblende type semiconductors.[5] However, this kind of band alignment with a large conduction band discontinuity (spike) contradicts the high performance of solar cells based on these interfaces. Evidently empirically developed interface preparation strongly modifies the band lineup in thin film chalcopyrite solar cells. The microscopic origin of the modification remains a key issue of future investigations.

In summary we have determined the valence band discontinuity between UHV-cleaved CuInS$_2$ surface and thermally evaporated CdS using synchrotron excited photoelectron spectroscopy. We found a value of $\Delta E_V = 0.6$ (± 0.1) eV, independent of CdS film thickness.

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