

# Photoemission study and band alignment of the $\text{CuInSe}_2(001)/\text{CdS}$ heterojunction

Cite as: Appl. Phys. Lett. **84**, 3067 (2004); <https://doi.org/10.1063/1.1712034>

Submitted: 27 December 2002 • Accepted: 24 February 2004 • Published Online: 13 April 2004

T. Schulmeyer, R. Hunger, A. Klein, et al.



View Online



Export Citation

## ARTICLES YOU MAY BE INTERESTED IN

[Flat conduction-band alignment at the  \$\text{CdS}/\text{CuInSe}\_2\$  thin-film solar-cell heterojunction](#)

Applied Physics Letters **79**, 4482 (2001); <https://doi.org/10.1063/1.1428408>

[Band alignment at the  \$\text{CdS}/\text{Cu}\(\text{In}, \text{Ga}\)\text{S}\_2\$  interface in thin-film solar cells](#)

Applied Physics Letters **86**, 062109 (2005); <https://doi.org/10.1063/1.1861958>

[Band offsets at the  \$\text{CdS}/\text{CuInSe}\_2\$  heterojunction](#)

Applied Physics Letters **63**, 2549 (1993); <https://doi.org/10.1063/1.110429>



Webinar  
Quantum Material Characterization  
for Streamlined Qubit Development



Register now

## Photoemission study and band alignment of the $\text{CuInSe}_2(001)/\text{CdS}$ heterojunction

T. Schulmeyer, R. Hunger,<sup>a)</sup> A. Klein, and W. Jaegermann

Darmstadt University of Technology, Institute of Materials Science, Surface Science Division,  
Petersenstrasse 23, D-64287 Darmstadt, Germany

S. Niki

National Institute of Advanced Industrial Science and Technology (AIST), Energy Electronics Institute,  
Thin Film Solar Cell Group, 1-1-1 Umezono, Tsukuba, Ibaraki 305-8568, Japan

(Received 27 December 2002; accepted 24 February 2004)

The contact formation of thin-film epitaxial  $\text{CuInSe}_2(001)$  with a physical-vapor-deposited CdS layer is presented in this work. Synchrotron-excited photoelectron spectroscopy was used for this investigation. The epitaxial  $\text{CuInSe}_2$  films contain a surface layer of reduced Cu stoichiometry similar to the ordered defect compound  $\text{CuIn}_3\text{Se}_5$ . A valence band offset of  $0.79 \pm 0.15$  eV has been determined for this heterojunction. The comparison to literature data indicates that neither surface orientation nor surface copper content have a major impact on the valence band offset of  $\text{CuIn}_3\text{Se}_5$ , respectively,  $\text{CuInSe}_2$  with CdS. © 2004 American Institute of Physics.  
[DOI: 10.1063/1.1712034]

$\text{CuInSe}_2$  with the corresponding alloys are promising absorber materials for the application in thin film solar cells. Common  $\text{Cu}(\text{In,Ga})\text{Se}_2$  solar cells are composed of a *p*-doped  $\text{Cu}(\text{In,Ga})\text{Se}_2$  layer, an *n*-doped CdS buffer layer and a transparent, highly *n*-doped ZnO film.<sup>1</sup> The dominant interface of the device is the  $\text{Cu}(\text{In,Ga})\text{Se}_2/\text{CdS}$  heterojunction, where the built-in potential separating the photogenerated carriers is established. Earlier investigations of the absorber-CdS heterointerface had shown that the interface is not formed between a stoichiometric  $\text{CuInSe}_2$  phase and CdS, but that the absorber surface is highly Cu deficient, forming a so-called ordered-defect compound (ODC) with approximate  $\text{CuIn}_3\text{Se}_5$  composition.<sup>2</sup> For this system, a valence band offset of 0.86 eV was determined. As the band gap of the ODC was determined to 1.3 eV, a conduction band offset of  $-0.26$  eV was deduced, which is favorable for the current transport through the device. On the other hand, investigations of UHV-cleaved  $\text{CuInSe}_2$  single crystals with (011) orientation had shown that the valence and conduction band offset between stoichiometric  $\text{CuInSe}_2$  and CdS amounts to 0.8 and  $-0.6$  eV, respectively.<sup>3</sup> The comparison of these experimental studies indicates, that the increase in band gap of 0.3–0.4 eV (Ref. 4) from stoichiometric  $\text{CuInSe}_2$  to the Cu-poor  $\text{CuIn}_3\text{Se}_5$  phase, is largely accommodated in a reduced conduction band offset with CdS. This is in contradiction to a recent theoretical study where the “natural” band offsets between CdS,  $\text{CuInSe}_2$ , and  $\text{CuIn}_3\text{Se}_5$  have been calculated.<sup>5</sup> It was found that the transition from  $\text{CuInSe}_2$  to  $\text{CuIn}_3\text{Se}_5$  should result in a lowering of the valence band maximum of 0.34 eV on an absolute energy scale, hence the valence band offsets with CdS should differ by this amount. The experimentally observed difference from Refs. 2 and 3, however, is less than 0.1 eV. With the background of divergent experimental and theoretical re-

sults we have reexamined the valence band offset between a Cu-poor surface phase of  $\text{CuInSe}_2$  and CdS using synchrotron-excited photoelectron spectroscopy.

For this *in situ* investigation we have exploited a type of single-crystalline substrate material: Se capped  $\text{CuInSe}_2(001)$  epilayers.  $\text{CuInSe}_2(001)$  epilayers were grown on GaAs(100) by molecular beam epitaxy (MBE) in a dedicated MBE system at the AIST. Details of the growth process were published earlier.<sup>6</sup> Immediately after growth, an amorphous selenium cap layer was deposited onto the clean  $\text{CuInSe}_2(001)$  film. The Se cap protects the  $\text{CuInSe}_2$  surface from oxidation and contamination during storage (and transport) in air. After reintroduction into the vacuum, the Se cap can be removed by thermal annealing higher than 150 °C. After decapping, the  $\text{CuInSe}_2$  films showed the RHEED pattern typical of Cu-poor epitaxial  $\text{CuInSe}_2(001)$ ,<sup>7</sup> which was identical to the RHEED pattern prior to Se capping. Details of the Se capping and decapping process are published elsewhere.<sup>8</sup>

The  $\text{CuInSe}_2(001)$  films employed for this study were grown in a bilayer process, where an initial Cu-rich  $\text{CuInSe}_2$  film is overgrown with In–Se only, and the global composition is turned to a slightly Cu-poor composition. Electron probe microanalysis measurements indicated a bulk composition of  $[\text{Cu}]/[\text{In}]=0.90$ . Al *K $\alpha$* -excited photoelectron spectroscopy of a decapped  $\text{CuInSe}_2(001)$  film indicated a  $[\text{Cu}]/[\text{In}]$  ratio of  $\sim 0.4$  ( $\pm 15\%$ ) of the surface. This corresponds to a surface cation ratio between the Cu-poor equilibrium phases  $\text{CuIn}_3\text{Se}_5$  and  $\text{Cu}_2\text{In}_4\text{Se}_7$ . This indicates the formation of a surface layer with a compared to the film bulk reduced copper content. We believe that this surface Cu deficiency is a result of the employed bilayer growth process. Recent structural evidence for the formation of a Cu-poor surface phase for the physical vapor deposition (PVD) in a multistep process of  $\text{CuInSe}_2$  is reported in Ref. 9. As we cannot unambiguously assign the surface material to a defined

<sup>a)</sup>Electronic mail: hunger@surface.tu-darmstadt.de

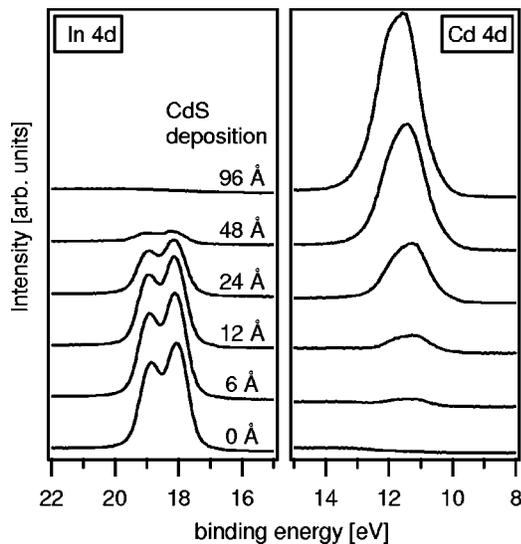


FIG. 1. In  $4d$  and Cd  $4d$  core level lines obtained for the stepwise deposition of CdS on CuInSe<sub>2</sub>(001).

phase, we will in the following denote it as Cu-poor CuInSe<sub>2</sub>(001).

The contact formation of CuInSe<sub>2</sub>(001) with CdS was investigated in an UHV system at the U49/2-PGM2 beamline of the BESSY II storage ring in Berlin. The surface analysis chamber was directly connected to a preparation chamber, which allowed for different surface preparation steps and transfer of samples without breaking the vacuum. The Se cap layer was removed by its thermal evaporation during annealing to 300 °C for 15 min. Thereafter, CdS was stepwise deposited onto the CuInSe<sub>2</sub> surface by PVD. The deposition rate was calibrated using a quartz microbalance. A photon energy of 95 eV was used to characterize the clean CuInSe<sub>2</sub> substrate and the specimen after every CdS deposition step by photoelectron spectroscopy. With this method the valence band offset can be determined as described elsewhere.<sup>10</sup>

In Fig. 1 the emission of the In  $4d$  core level of the substrate and the Cd  $4d$  level of the overlayer after different CdS evaporation steps are shown. The In  $4d$  signal is attenuated with increasing CdS coverage. Correspondingly, the Cd  $4d$  intensity increases. The core level line shapes do not change with coverage and hence, do not indicate interface chemical shifts. Substrate signals are no longer observed for the largest investigated coverage of 96 Å, i.e., the CdS film is closed and completely covers the substrate.

In Fig. 2 the valence band emission structures after different CdS evaporation steps are displayed. The spectrum of the clean CuInSe<sub>2</sub> substrate material clearly shows a reduced intensity of the Cu  $3d$  emission at about 3.5 eV, which indicates the reduced surface Cu content relative to the stoichiometric CuInSe<sub>2</sub> composition.<sup>11</sup> The spectrum of the largest coverage (96 Å) shows the typical emission features known for polycrystalline CdS.

To determine the valence band offset, it is necessary to assign the difference between the core levels and the valence band maximum (VBM). The VBM was determined by fitting a straight line to the photoemission onset at low binding energy values. The core level peaks were fitted using mixed Gauss-Lorentzian broadened Voigt profiles of spin-orbit split doublets. All core levels could be fitted with a fixed line shape

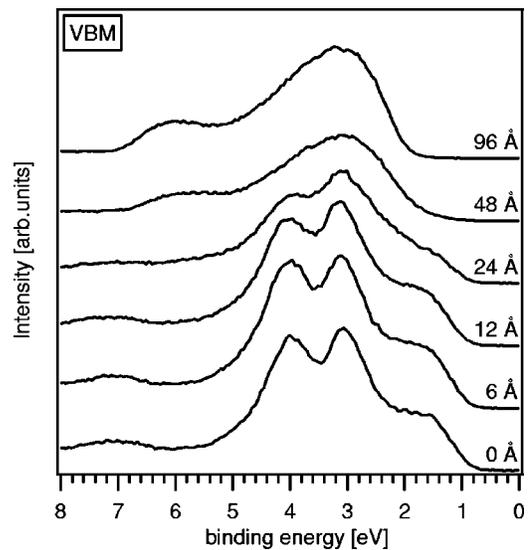


FIG. 2. Valence band spectra ( $h\nu=95$  eV) at different evaporation steps. The first spectrum is from the clean, decapped CuInSe<sub>2</sub>(001) surface and the last from the closed CdS layer.

and a constant Gauss to Lorentz ratio, hence interface reactions with the deposition steps are not indicated. The binding energy of the In  $4d$  peak with respect to VBM has been determined to  $E_B^{\text{VBM}}=17.22\pm 0.07$  eV. The binding energy of the Cd  $4d$  peak is  $E_B^{\text{VBM}}=9.49\pm 0.07$  eV. Using these data, the evolution of the position of the VBM relative to the Fermi level,  $E_F-E_{\text{VBM}}$ , was extracted from the core level positions in the course of CdS deposition. The decapped CuInSe<sub>2</sub>(001) and the thick (96 Å) CdS surface were used as reference points. For the analogous studies on and polycrystalline CuIn<sub>3</sub>Se<sub>5</sub><sup>2</sup> and cleaved CuInSe<sub>2</sub>(011)<sup>3</sup> binding energies of In  $4d$ /Cd  $4d$  relative to VBM of 17.19/9.41 eV and 17.3/9.5 eV were measured. The agreement with the literature data is reasonable.

Figure 3 shows the evolution of  $E_F-E_{\text{VBM}}$  for the CuInSe<sub>2</sub>(001) substrate and the CdS overlayer as derived from the In  $4d$  and the Cd  $4d$  peaks. Starting from  $E_F-E_{\text{VBM}}=0.8$  eV for the clean CuInSe<sub>2</sub>(001) surface, the Fermi level moves closer to the conduction band with increasing CdS coverage. This is due to the additional band bending in the CuInSe<sub>2</sub> induced by the CdS contact formation. A corresponding shift of the Fermi level is observed

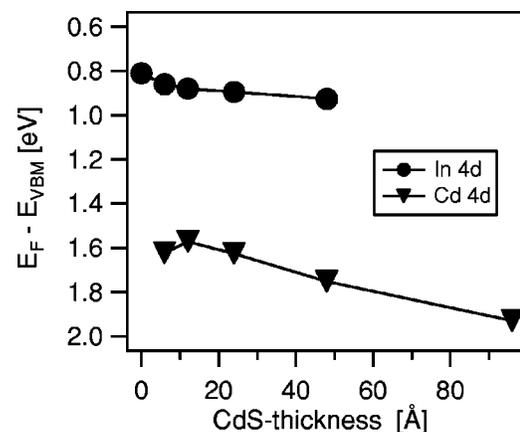


FIG. 3. Distance between the Fermi level and the valence band maximum as derived from the investigated core levels In  $4d$  and Cd  $4d$ .

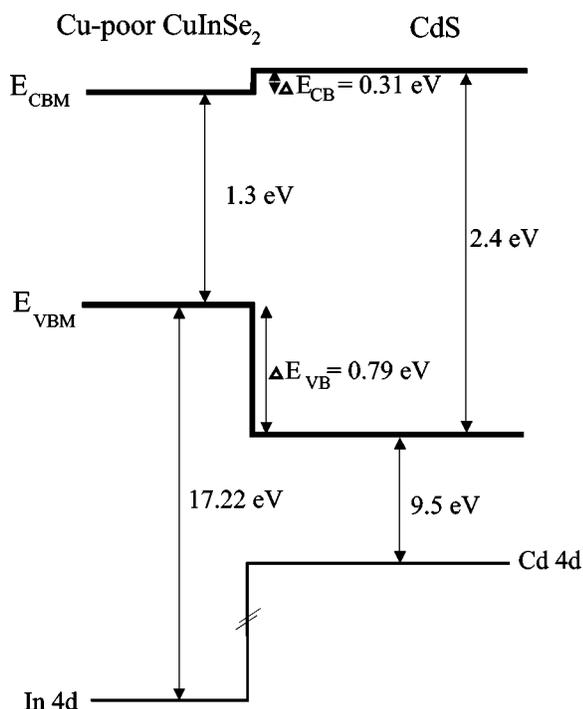


FIG. 4. Band energy diagram of the heterojunction between the Cu-poor  $\text{CuInSe}_2(001)$  surface and CdS. The valence band offset is determined to 0.79 eV.

within the CdS for film thicknesses larger than 12 Å which is due to the decrease of depletion with increasing CdS film thickness. For the first two deposition steps the CdS VBM appears to move in the opposite direction. The origin of this behavior is not clear. Possibly, this is effected by an overlayer–substrate interaction, e.g., exchange reactions at the phase boundary modifying the binding energy of Cd 4*d* with respect to the VBM. This process, however, occurs in less than stoichiometric amounts, as otherwise it should be reflected in the core level line shapes. The process appears to be completed for a film thickness around 12 Å.

The valence band offset between  $\text{CuInSe}_2(001)$  and CdS,  $\Delta E_{VB}$ , is evident from Fig. 3 as difference between the position of the valence band edges. The numerical values for  $\Delta E_{VB}$  for the data at 6, 12, 24, and 48 Å coverage are 0.73, 0.69, 0.75, and 0.83 eV, respectively. Due to the overlayer–substrate interaction for 6 and 12 Å coverage, the  $E_F - E_{VBM}$  figures for CdS are less reliable and we derive the final  $\Delta E_{VB}$  value by averaging over the 24 and 48 Å data points only. Thereby, we determine as valence band offset between the Cu-poor  $\text{CuInSe}_2(001)$  surface and CdS  $\Delta E_{VB} = 0.79 \pm 0.15$  eV. The error margin of 0.15 eV reflects not only the principal experimental uncertainty but as well the scatter of the individual data points. The complete band energy diagram of the Cu-poor  $\text{CuInSe}_2(001)/\text{CdS}$  heterojunction is shown in Fig. 4. One disadvantage of the photoelectron spectroscopy is the missing information of the conduction band minimum. By adding the band gap to the value of the valence band maximum, the conduction band minimum can be determined. A band gap of 1.3(1) eV for the Cu-poor

$\text{CuInSe}_2$  surface<sup>2</sup> and a band gap of 2.4 eV of the CdS layer has been assumed for the given figure. With these values the conduction band offset can be calculated to  $\Delta E_{CB} = 0.31 \pm 0.25$  eV. This value is in good correspondence to previously published values of Cu-deficient  $\text{CuInSe}_2$  absorber surfaces.<sup>2,4</sup>

Comparing the  $\Delta E_{VB}$  values for the Cu-poor epitaxial  $\text{CuInSe}_2(001)$  surface ( $0.79 \pm 0.15$  eV) to the previously published literature data on polycrystalline  $\text{CuIn}_3\text{Se}_5$  surface with preferred (112) orientation<sup>2</sup> ( $0.86 \pm 0.15$  eV), and to a stoichiometric cleaved  $\text{CuInSe}_2(011)$  surface<sup>3</sup> ( $0.8 \pm 0.1$  eV), two conclusions are to be drawn:

- (i) The surface orientation evidently has only a minor effect on the valence band offset.
- (ii) Experimentally, the valence band offset is independent of the surface Cu content.

The calculation of natural band offsets,<sup>5</sup> however, suggests the reduction of the valence band offset by 0.34 eV when going from  $\text{CuInSe}_2$  to  $\text{CuIn}_3\text{Se}_5$ . The discrepancy between experimental data and natural band offsets suggests the formation of interface dipole of differing magnitude for the  $\text{CuInSe}_2/\text{CdS}$  and  $\text{CuIn}_3\text{Se}_5/\text{CdS}$  interfaces, respectively.

In summary, the measured valence band offset of 0.79 eV is comparable to the valence band offset of (011) single crystal  $\text{CuInSe}_2$  and of polycrystalline  $\text{CuInSe}_2$  thin films. The orientation of the absorber layer evidently has no significant influence on the valence band offset. In comparison to the single crystal without the ODC surface, the increased band gap has no influence of the valence band offset. The smaller conduction band offset is an evident advantage of the ODC– $\text{CuIn}_3\text{Se}_5/\text{CdS}$  heterojunction.

The support for the experiments at BESSY by D. Schmeisser and P. Hoffmann is gratefully acknowledged. During his stay at the AIST, R.H. received a grant from the Science and Technology Agency (MITI, Japan).

<sup>1</sup>U. Rau and H. Schock, Appl. Phys. A: Mater. Sci. Process. **69**, 131 (1999).

<sup>2</sup>D. Schmid, M. Ruckh, F. Grunwald, and H. Schock, J. Appl. Phys. **73**, 2902 (1993).

<sup>3</sup>T. Löher, W. Jaegermann, and C. Pettenkofer, J. Appl. Phys. **77**, 731 (1995).

<sup>4</sup>M. Morkel, L. Weinhardt, B. Lohmüller, C. Heske, and E. Umbach, Appl. Phys. Lett. **79**, 4482 (2001).

<sup>5</sup>S. Zhang, S.-H. Wei, and A. Zunger, Phys. Rev. B **57**, 9642 (1998).

<sup>6</sup>S. Niki, Y. Makita, A. Yamada, A. Obara, O. Igarashi, S. Misawa, M. Kawai, H. Nakanishi, Y. Taguchi, and N. Kutsuwada, Sol. Energy Mater. Sol. Cells **35**, 141 (1994).

<sup>7</sup>S. Niki, Y. Makita, A. Yamada, O. Hellman, P. J. Fons, A. Obara, Y. Okada, R. Shioda, H. Oyanagi, T. Kurafuji, S. Chichibu, and H. Nakanishi, J. Cryst. Growth **150**, 1201 (1995).

<sup>8</sup>R. Hunger, T. Schulmeyer, A. Klein, W. Jaegermann, K. Sakurai, A. Yamada, P. Fons, K. Matsubara, and S. Niki, Surf. Sci. Lett. (in press).

<sup>9</sup>I. M. Kötschau and H. W. Schock, J. Phys. Chem. Solids **64**, 1559 (2003).

<sup>10</sup>*Heterojunction Band Discontinuities*, edited by F. Capasso and G. Margaritondo (North-Holland, Amsterdam, 1987).

<sup>11</sup>T. Löher, A. Klein, C. Pettenkofer, and W. Jaegermann, J. Appl. Phys. **81**, 7806 (1997).