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Flat conduction-band alignment at the CdS/CuInSe$_2$ thin-film solar-cell heterojunction

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By combining ultraviolet and x-ray photoelectron spectroscopy with inverse photoemission spectroscopy, we find that the conduction-band alignment at the CdS/CuInSe$_2$ thin-film solar-cell heterojunction is flat (0.0 ± 0.2 eV). Furthermore, we observe a valence-band offset of 0.8 ± 0.2 eV. The electronic level alignment is dominated by (1) an unusually large surface band gap of the CuInSe$_2$ thin film (1.4 eV), (2) by a reduced surface band gap of the CdS overlayer (2.2 eV) due to intermixing effects, and (3) by a general influence of the intermixing on the chemical state near the interface. © *2001 American Institute of Physics.* [DOI: 10.1063/1.1428408]

Thin-film solar cells on the basis of CuInSe$_2$ (CISe) have reached a high level of performance, both on a laboratory scale (conversion efficiencies up to 18.8%) as well as in large-area modules (12.1% for 3651 cm^2).[1] A further optimization calls for the establishment of detailed electronic models to understand the interplay of the different layers of the cell and their impact on the electronic structure and performance.

One of the crucial parameters in modeling the electronic properties is the conduction-band alignment at the interfaces of the solar cell, in particular at the CdS/CISe interface. However, no direct determination of the conduction-band offset (CBO) has hitherto been reported, mostly because it is difficult to investigate the unoccupied conduction-band states. Furthermore, CISe solar cells constitute a nonideal system with, e.g., inhomogeneities, contaminations, and intermixing effects. A number of authors have presented photoemission investigations (PES) to determine the valence-band offset (VBO) and have then employed literature band-gap values to deduce the CBO indicating a ''spike'' in the conduction band [i.e., the conduction-band minimum (CBM) of CdS lies above the conduction-band minimum of CISe, ''CBO>0'']. A spike has consequently been incorporated into most of the electronic models presently available.[2–5] It is the purpose of this letter to demonstrate that such an approach is not applicable in the case of *real* CdS/CISe solar-cell interfaces, at least not for those prepared by chemical bath deposition (CBD) of CdS. In contrast, by studying the conduction-band minimum directly with inverse photoemission spectroscopy (IPES), we find that a step-free description has to be adopted. This finding makes it much easier to understand the achieved high efficiencies.

The CBO at the CdS/CISe interface has been a topic of discussion ever since the first proof-of-principle demonstration of CISe solar cells.[6] At that point, it was believed that a detrimental spike in the conduction band could be ruled out, and first indirect experimental results [CBO between -0.08 and -0.18 eV (Ref. 7)] supported this belief. Since then, a number of PES experiments have been performed for a variety of differently prepared CdS/CISe samples. These investigations determined a VBO and then deduced a CBO from suitable reference gap values for CISe and CdS,[8–11] indicating a spike of 0.2–0.3 eV (Refs. 8 and 11) up to 0.7 eV.[10] Two first-principle calculations also derived a spike [approximately 0.3 eV (Refs. 9 and 12)]. When Niemegeers and co-workers,[13] found that, even with a spike, the simple assumption of thermionic emission across the junction can explain an unimpeded electron transport in an n^+p structure (as in the present case) a spike, was generally accepted, notwithstanding the fact that Kronik *et al.* in the same year published a surface photovoltage spectroscopy investigation of CBD–CdS/Cu(In$_{0.91}$,Ga$_{0.09}$)Se$_2$, suggesting a flat conduction-band alignment (0.08 ± 0.10 eV).[14] Liu and Sites simulated the transport properties for the case of an In-rich CISe surface (as in our investigation): the efficiency and fill factor dropped significantly for spikes larger than 0.1 eV and for cliffs (''CBO<0'') more negative than -0.4 eV.[15] Furthermore, Niemegeers and co-workers could find a consistent explanation of their experimental capacitance data only if the spike is assumed to be smaller than 0.11 eV.[2]

For the present experiments, He I and He II irradiation [ultraviolet photoelectron spectroscopy (UPS)] as well as Mg $K\alpha$ excitation [x-ray photoelectron spectroscopy (XPS)] were used. For IPES experiments, a Cicacci-type electron source and a Dose-type detector with a SrF$_2$ window and Ar:I$_2$ filling were employed. Band gaps are determined by UPS and IPES with a linear extrapolation of the leading edges, resulting in an accuracy of better than ± 0.15 eV for the derived band gap. The band offsets given in this letter are exact to ± 0.2 eV. The samples were prepared by rapid ther-

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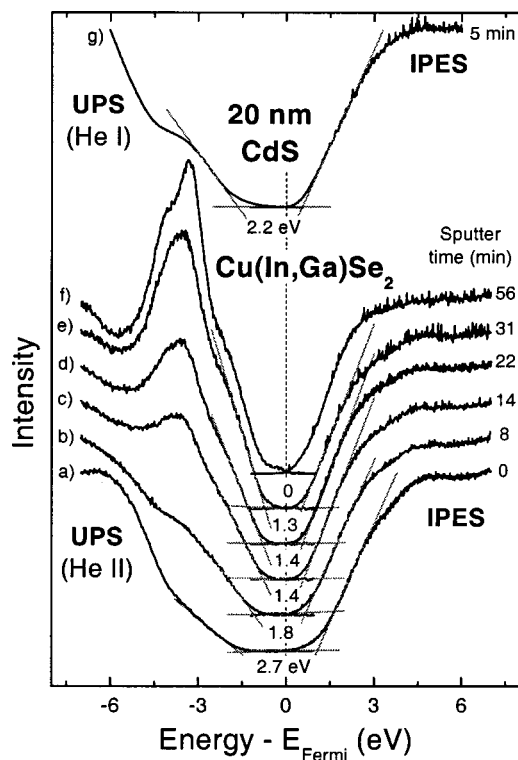[b]Electronic mail: heske@physik.uni-wuerzburg.de

FIG. 1. UPS and IPES spectra of a CuInSe₂ thin-film solar-cell absorber and of a 20 nm CBD-CdS/CuInSe₂ interface sample. The spectra were taken after subsequent Ar⁺-ion sputter steps, as listed on the right-hand side. Gray lines indicate the linearly extrapolated band edges; the determined band gaps are given in the center.

mal annealing of elemental layers on Mo-coated soda-lime glass and by subsequent chemical bath deposition of CdS. Note that the CISe layers also contain Ga, but show only trace amounts near the CISe surface.

CISe absorber surfaces taken from a cost-efficient production process are naturally covered with surface contaminants. As can be seen in Fig. 1, this can obscure the electronic structure observed with surface-sensitive methods. He II UPS valence-band edges and IPES conduction-band edges are shown on a common energy scale. The lower pair of spectra (a) reveals a surface band gap of about 2.7 eV, which is entirely ascribed to the "band gap" of the surface contaminants. To obtain a realistic value for the CISe surface band gap, we have employed short mild Ar⁺-ion sputter steps (500 eV, low and varying incidence angles, 1 μA/cm²). As shown in Fig. 1 [spectra (b)–(f)], this treatment "reduces" the surface band gap after a short sputter time to a constant value of about 1.4 eV, and XPS proves that the contaminants have essentially been removed. Note that it is well known—and also corroborated by our XPS data—that the surface contaminants are also removed during the CBD process. Hence, the surface band gap derived after the sputter treatment is expected to be a good approximation of the CISe band gap directly at the CdS/CISe interface. For long sputter times (e.g., 1 h) a Fermi edge evolves, indicating the formation of metallic species on the surface.[16,17] This is consistent with common knowledge that intense sputter treatments can substantially influence the stoichiometry and other surface properties.[16,18] It is noteworthy that for sputtering times of 14 min and above the intensities of In and Se XPS lines reach a plateau, while the Cu intensity rises continuously. This indi-

cates that after 14 min both the influence of the surface contamination as well as the sputter-induced artifacts are minimized. We, hence, associate the observed band-gap plateau of 1.4 ($\pm$0.15) eV with the CISe surface band gap, the higher gaps at the initial stages with the gap of the contamination layer, and the smaller gap values (1.3–0 eV) for long sputter times with sputter-damaged and stoichiometrically altered CISe surfaces.

The finding of a 1.4 eV surface gap for CISe is not entirely surprising, because an In-rich surface layer with increased band gap has been under discussion for quite some time.[8,19] The XPS data clearly show that the surfaces investigated in our study are indeed In rich (Cu poor); hence, a band gap of 1.4 eV is completely consistent with such a layer. This finding also reveals one of the shortfalls of the above-discussed previous approach (i.e., to determine the VBO and to estimate the CBO from reference band gaps): compared to the CISe bulk band gap of 1.0 eV, the current finding would reduce the such-derived CBO by about 0.4 eV.

Moreover, we find that the band gap of CdS is also different from the "expected" reference value (2.4 eV). From the upper pair of spectra (g) in Fig. 1, we derive a surface band gap of 2.2 eV ($\pm$0.15 eV) for the standard CBD-CdS film of 20 nm thickness (the sample was sputtered for 5 min and He I excitation was chosen to avoid satellite structures from the Cd 4d levels). We ascribe this band-gap reduction to a Se diffusion, which leads to the formation of a Cd(S,Se) film.[20] This finding is corroborated by our XPS spectra (not shown), where Se shows by far the least signal attenuation with CdS film thickness. Note that the Se content is possibly even higher close to the interface, which would lead to an even smaller band gap. This would shift the conduction-band offset towards smaller or more negative values. However, since the intermixing processes lead to a "smeared-out" band alignment, we expect this effect to have only a small impact on the determined CBO.

Having thus identified some of the shortcomings in determining the CBO based on reference values, we now derive the CBO directly from our IPES and XPS data. Note that here the band-gap values are not directly utilized for the conduction-band-offset determination: in a first step, only the offset between the CBMs of a CISe absorber surface and of a 20 nm CdS/CISe sample is probed with IPES. In a second step, this offset is corrected with the additional band bending induced by the interface formation process, both in CISe and in CdS. This correction is based on XPS core-level shifts derived from a comparison between line positions observed for a bare CISe absorber, a thin CdS overlayer on a CISe absorber, and a thick CdS film. In our case, four samples with varying CdS film thickness were used.

For the first step, we compare the IPES spectra (c) and (g) of Fig. 1. While for CISe the CBM is 0.6 eV above the Fermi energy, we find this separation to be 0.4 eV for CdS. This suggests—in crude approximation—a cliff alignment of -0.2 eV without taking band bending into account. For the second step, we have investigated the most intense core levels with XPS, as listed in Table I. The various combinations of CISe and CdS core levels are given along with the VBO and CBO values determined from UPS (VBO) and IPES (CBO) *after* a core-level-shift correction. The results can be

TABLE I. Valence-band offset (VBO) and conduction-band offset (CBO) based on the UPS- and IPES-derived band edges of Fig. 1 and on an interface-induced band-bending correction derived from XPS core-level shifts. The table lists several combinations of accessible core levels of $CuInSe_2$ and CdS and is grouped by substrate element.

CuInSe$_2$ level	CdS level	VBO	CBO
Cu $2p_{3/2}$	Cd $3d_{3/2}$	0.99	−0.23
Cu $2p_{3/2}$	Cd $4d_{3/2}$	0.98	−0.22
Cu $2p_{3/2}$	S $2p_{3/2}$	0.91	−0.15
In $3d_{3/2}$	Cd $3d_{3/2}$	0.65	+0.11
In $3d_{3/2}$	Cd $4d_{3/2}$	0.64	+0.12
In $3d_{3/2}$	S $2p_{3/2}$	0.57	+0.19
In $4d_{5/2}$	Cd $3d_{3/2}$	0.71	+0.05
In $4d_{5/2}$	Cd $4d_{3/2}$	0.70	+0.06
In $4d_{5/2}$	S $2p_{3/2}$	0.63	+0.13
Se $3p_{3/2}$	Cd $3d_{3/2}$	0.80	−0.04
Se $3p_{3/2}$	Cd $4d_{3/2}$	0.79	−0.03
Se $3p_{3/2}$	S $2p_{3/2}$	0.72	+0.04
Se $3d_{5/2}$	Cd $3d_{3/2}$	0.79	−0.03
Se $3d_{5/2}$	Cd $4d_{3/2}$	0.78	−0.02
Se $3d_{5/2}$	S $2p_{3/2}$	0.71	+0.05

grouped according to the substrate element (i.e., Cu, In, and Se) and give consistent values within each subgroup. The CBO with Cu-based corrections is about −0.2 eV, for In-based corrections about +0.1 eV, and for Se-based corrections 0.0 eV. We ascribe the observed variation between the subgroups to the intermixing processes at the CdS/CISe interface: in addition to a significant S–Se exchange, we also observe an In diffusion into the CdS film.[20] Other authors report other exchange processes.[21] Hence, some of the atoms probed in the XPS spectra are bound in a different chemical environment, giving rise to chemical shifts in addition to the band-bending effects to be investigated. Nevertheless, we find that the conduction-band offset is certainly not larger than 0.1 eV, and we can give a realistic average value of $\overline{CBO} = 0.0(\pm 0.2)$ eV. This clearly rules out a significant spike in the conduction band. Note that the observed average valence-band offset $\overline{VBO} = 0.8(\pm 0.2)$ eV is identical or close to many VBOs determined in other PES experiments. Apparently, it is the assumption of incorrect band-gap values (for the real solar-cell system) which has led to the inclusion of a spike into the various solar-cell models.

The experimental findings are summarized in Fig. 2. We observe a vanishing average CBO of 0.0 (± 0.2) eV and an average VBO of 0.8 (± 0.2) eV. The electronic band alignment is strongly influenced by (surface) band gaps for CISe and (CBD-deposited) CdS, which deviate from reference bulk values, and by the impact of intermixing effects at the CdS/CISe interface. Based on our results, a spike in the conduction band can be ruled out, and the models describing and simulating the macroscopic solar-cell performance will need to be reconsidered in view of nonreference band-gap values, a flat conduction-band alignment, and intermixing.
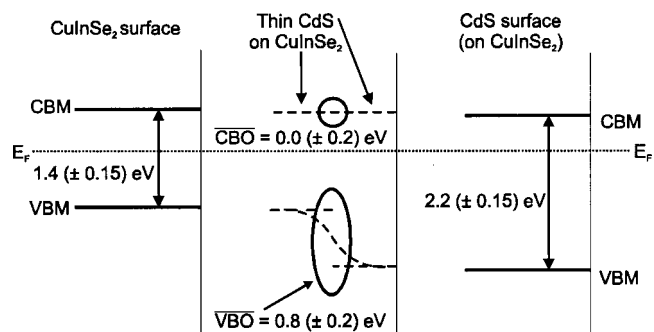
FIG. 2. Schematic summary of the experimental band alignment results. The left and right parts of the figure represent the level alignment at the surfaces of $CuInSe_2$ and CdS films, respectively (solid lines). The central part displays the level alignment directly at the interface (dashed lines), which, in addition to the energetic positions far away from the interface, also takes a core-level-based band-bending correction as well as interdiffusion into account. (CBM and VBM denote the conduction-band minimum and valence-band maximum, respectively. Similarly, $\overline{CBO}$ and $\overline{VBO}$ represent the averaged conduction- and valence-band offsets.)

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