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Band offsets at the CdS/CuInSe₂ heterojunction

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The traditional explanation for the successful electron-hole separation in CdS/CuInSe₂ solar cells rests on the assumption of a type-II band lineup: The conduction-band minimum is assumed to be on the CdS window while the valence-band maximum is assumed to be localized on the CuInSe₂ absorber. This picture of negative conduction-band offset $\Delta E_c < 0$ was supported by the electron affinity rule, but was sharply contradicted by the more recent photoemission experiments of Nelson *et al.* for CdS/CuInSe₂ yielding $\Delta E_c = +1.08$ eV. Our first principles calculations yield for CdS/CuInSe₂ $\Delta E_c = +0.31$ eV, hence, a type-I band alignment. We challenge the published experimental value as being in error and point to the need of revising current solar cell device models that assume $\Delta E_c < 0$.

Solar cells based on *p*-CuInSe₂ absorber layers ($E_g = 1.04$ eV) and *n*-CdS window layers ($E_g = 2.42$ eV) have developed rapidly from 5% efficiency in 1974¹ to about 15% at present.² Despite this rapid progress, the qualitative nature of the band alignment between CdS and CuInSe₂ remains a mystery: The traditional view³ is that in such cells a heterojunction is formed between *p*-CuInSe₂ and *n*-CdS, that the conduction-band minimum (CBM) is on CdS (negative conduction-band offset $\Delta E_c < 0$), and that the valence-band maximum (VBM) is on CuInSe₂ (positive valence-band offset $\Delta E_v > 0$). This "type-II" band alignment was thought to be essential for electron transport from CuInSe₂ to CdS, and to eliminate the unfavorable conduction-band spike which would have resulted from $\Delta E_c > 0$. This picture was initially supported by the electron affinity (χ) rule [$\chi(\text{CdS}) \approx 4.86$ eV,⁴ $\chi(\text{CuInSe}_2) \approx 4.58$ eV,⁵ so $\Delta E_c \approx -0.28$ eV], as well as by the zero-temperature extrapolation of the open-circuit voltage of a solar cell⁶ ($\Delta E_c = -0.08$ eV). Given the large uncertainties of such estimates, Turowski *et al.*^{7,8} measured, using synchrotron-radiation photoemission, the valence-band offset ΔE_v of crystalline *X*/CuInSe₂ and *X*/CdS for *X*=Si⁷ and *X*=Ge.⁸ By using the transitivity rule, assumed previously⁹ to be ± 0.15 eV accurate, they derived that for CdS/CuInSe₂ $\Delta E_c = -0.18$ eV and $\Delta E_v = 1.56$ eV,⁷ amended later⁸ to $\Delta E_c = -0.03$ and $\Delta E_v = 1.41$ eV,⁸ both in qualitative agreement with the paradigm $\Delta E_c < 0$. Nelson *et al.*¹⁰ directly measured, for the first time, the band offset of crystalline CdS/CuInSe₂ using core-level synchrotron-radiation soft x-ray photoemission spectroscopy, finding a large and positive $\Delta E_c = 1.08$ eV (and $\Delta E_v = 0.30$ eV). This unexpected result places the CBM of CuInSe₂ absorber below that of the CdS window, leading to a type-I band alignment which invalidates the traditional view^{3,6-8} on electron transport in this system.

Uncertainties¹¹ regarding the stoichiometry of the deposited CdS film and the mechanical integrity of the CdS/CuInSe₂ interface lead us earlier¹² to examine the internal consistency of these results. To this end, we have first predicted theoretically and then carefully measured the band offset of the simpler, *common-anion* ZnSe/CuInSe₂ system.¹² Both the calculations and the measurements were done using the same ingredients, namely finding the core

(C) level to VBM separation in (i) the pure chalcopyrite $\Delta E_{\text{VBM,C}}^{ABX_2} = E_{\text{VBM}}^{ABX_2} - E_C^{ABX_2}$, in (ii) the pure II-VI partner $\Delta E_{\text{VBM,C}}^{DY} = E_{\text{VBM}}^{DY} - E_C^{DY}$, and obtaining (iii) the difference $\Delta E_{\text{core}} = E_C^{DY} - E_C^{ABX_2}$ between core levels at the *DY/ABX₂* interface. Combining these three steps gives

$$\Delta E_v = \Delta E_{\text{VBM,C}}^{ABX_2} - \Delta E_{\text{VBM,C}}^{DY} - \Delta E_{\text{core}} \quad (1)$$

The three terms of Eq. (1) were calculated using the local density formalism, as implemented by the highly precise linear augmented plane wave (LAPW) method.¹³ We predicted (Fig. 1)¹² $\Delta E_v(\text{ZnSe/CuInSe}_2) = 0.70 \pm 0.05$ eV for the relaxed interface (thus invalidating the common-anion rule which would have led to $\Delta E_v \sim 0$). Subsequent careful experiments¹² led to $\Delta E_v = 0.70 \pm 0.15$ eV for the system. Encouraged by these tests, we set up to calculate the more difficult case of a three-cation *two-anion* CdS/CuInSe₂ system. The results reported in some detail below are $\Delta E_v = 1.07 \pm 0.05$ eV for the relaxed interface, leading to $\Delta E_c = 0.31 \pm 0.05$ eV (Fig. 1). This should be compared to the experimental results of Nelson *et al.*¹² $\Delta E_v = 0.30$ and $\Delta E_c = 1.08$ eV. While both theory and experiment agree that $\Delta E_c > 0$ (hence, a type-I band alignment) in defiance of the traditional expectation,^{3,6-8} the large quantitative discrepancy seemed to us to warrant a reexamination of the *experimental* results for CdS/CuInSe₂. Recently, Niles and co-workers¹⁴ responded to this challenge and performed

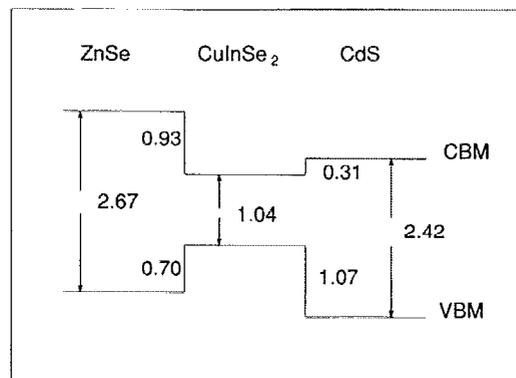


FIG. 1. Schematic of the calculated band lineup of the ZnSe/CuInSe₂ and CdS/CuInSe₂ heterojunctions. Energies are in eV.

careful synchrotron-radiation measurements on high quality interfaces of CdS/CuInSe₂. They find $\Delta E_v = 0.9 \pm 0.2$ and $\Delta E_c = 0.5 \pm 0.2$ eV, in good agreement with the theoretical predictions. Both experiment and theory then imply that the CBM and the VBM are on CuInSe₂ (type-I alignment), so the traditional explanation of electron transport^{3,6-8} must be incorrect. Possible explanations of this conflict are discussed below. In what follows we (i) explain the basic elements of the calculation, (ii) clarify why ZnSe has a smaller ΔE_v with CuInSe₂ than CdS, (iii) predict the strain dependence of ΔE_v , and (iv) show that the VBM wave function is localized on the CuInSe₂ side while the CBM wave function is delocalized on both heterojunction partners (despite $\Delta E_c > 0$).

The quantities appearing in Eq. (1) were obtained by performing three self-consistent and fully relativistic (i.e., including spin-orbit effects) LAPW¹³ band structure calculations for CdS, CuInSe₂, and the superstructure (CuInSe)₂(CdS)₄ which contains the active interface. Calculation were performed both for relaxed (incoherent) interfaces and for strained interfaces. Using in Eq. (1) the *cation* core levels as reference we find for the relaxed interface $\Delta E_v = 1.09$ eV, whereas using the *anion* core levels as reference gives $\Delta E_v = 1.05$ eV. The difference reflects the limit of accuracy of this calculation. Only ΔE_v is calculated directly, while ΔE_c is obtained as $\Delta E_c = E_g(\text{CdS}) - E_g(\text{CuInSe}_2) - \Delta E_v$. This gives for the relaxed interface $\Delta E_v = 1.07 \pm 0.05$ eV and $\Delta E_c = 0.31 \pm 0.05$ eV. These results are depicted in Fig. 1 and are in good agreement with the more recent determination of Niles *et al.*,¹⁴ $\Delta E_v = 0.9 \pm 0.2$ eV and $\Delta E_c = 0.5 \pm 0.2$ eV, in which high quality interfaces were produced.

To investigate the effect of strain, we calculated ΔE_v also for the *coherent* interface of CdS on a CuInSe₂ (112) substrates (i.e., 1% compression of CdS). We find that the VBM and CBM of CdS move *up* due to strain by 0.06 and 0.03 eV, respectively, decreasing ΔE_v by 0.06 eV and increasing ΔE_c by 0.03 eV. For ZnSe/CuInSe₂ we find that coherence with CuInSe₂ substrate (i.e., 2% expansion of ZnSe) moves the VBM of ZnSe up by 0.10 eV while the CBM moves *down* by 0.13 eV.

To understand the physical cause and chemical trends in the valence-band offsets in these systems, consider first the common-anion case of ZnSe/CuInSe₂ for which the calculated and measured ΔE_v value¹² is ~ 0.7 eV. Recall that if the VBM wave function in these semiconductors were composed entirely of *p* orbitals (as simplified band structure arguments would suggest), one would expect by the common anion rule that $\Delta E_v \approx 0$. Accurate band structure calculations for chalcopyrites¹⁵ and for II-VI compounds^{16,17} suggest, however, mixing of *cation d* character into the VBM. This reflects the interaction between anion *p* orbitals (with initial energy $\epsilon_{a,p}^0$) and cation *d* orbitals (with initial energy $\epsilon_{c,d}^0$). This interaction repels the VBM upwards by $R^{p-d} \sim V_{p-d}^2 / (\epsilon_{a,p}^0 - \epsilon_{c,d}^0)$, where V_{p-d} is the interaction matrix element. This repulsion leads to a band gap narrowing,¹⁵ and to a reduction in the spin-orbit splitting in chalcopyrites relative to binary II-VIs.¹⁶ Note that this repulsion increases as $(\epsilon_{a,p}^0 - \epsilon_{c,d}^0)$ is reduced and as the

TABLE I. Breakdown of the total valence band offset ΔE_v to pure *p* orbital contribution (in the absence of *p-d* coupling) and a *p-d* repulsion term [Eq. (2)], all in eV. A denotes anion and C denotes cation.

Quantities	ZnSe/CuInSe ₂	CdS/CuInSe ₂
	C1=Zn, C2=Cu A1=Se, A2=Se	C1=Cd, C2=Cu A1=S, A2=Se
$E_2^p - E_1^p$	0.02	0.45
R_{A1-C1}^{p-d}	0.34	0.40
R_{A2-C2}^{p-d}	1.02	1.02
$R_{A2-C2}^{p-d} - R_{A1-C1}^{p-d}$	0.68	0.62
ΔE_v	0.70	1.07

orbital coupling V_{p-d} is enhanced. Hence, we expect different repulsions in each side of the interface. This will contribute to ΔE_v . The total valence-band offset between a semiconductor with anion *A1* and cation *C1* and a lattice-matched semiconductor with anion *A2* and cation *C2* can then be thought of as consisting of a piece due to *p* orbital energy difference at the VBM (in the absence of *p-d* interaction), and a piece due to different *p-d* repulsions in the two materials:

$$\Delta E_v = (E_2^p - E_1^p) + (R_{A2-C2}^{p-d} - R_{A1-C1}^{p-d}). \quad (2)$$

The left-hand side of Eq. (2) was calculated directly from Eq. (1) as described above. The first term on the right hand side of Eq. (2) was obtained by repeating the LAPW calculations, disabling however the *p-d* coupling. Table I shows the result of the decomposition of Eq. (2). Figure 2 depicts the calculated wave function square of the VBM state on both sides of the CdS/CuInSe₂ interface. We see that: (i) the common anion rule ($E_1^p \approx E_2^p$ for equal anions $A1=A2$) works only *in the absence* of *p-d* coupling. (ii) The *p-d* repulsion in CuInSe₂ is much larger than in the II-VIs since the Cu 3*d* has the smallest binding energy (small $\epsilon_{a,p}^0 - \epsilon_{c,d}^0$) and its orbitals are more delocalized (large V_{p-d}). (iii) $\Delta E_v \neq 0$ in ZnSe/CuInSe₂ results almost entirely from *p-d* coupling. (iv) $\Delta E_v(\text{CdS/CuInSe}_2)$ exceeds $\Delta E_v(\text{ZnSe/CuInSe}_2)$ mostly because of the larger binding energy of the S 3*p* orbital in CdS relative to the Se

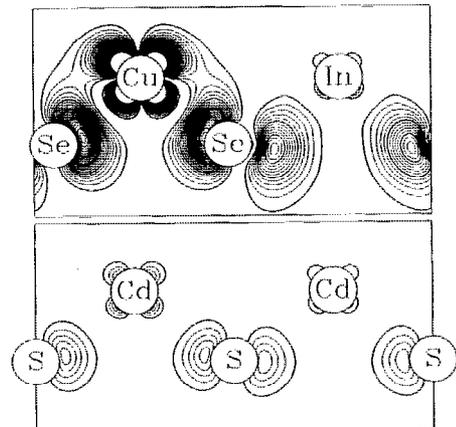


FIG. 2. Wave function square of the VBM state at both sides of the CdS/CuInSe₂ heterojunction. Upper panel: Center layer of CuInSe₂, lower panel: Center layer of CdS.

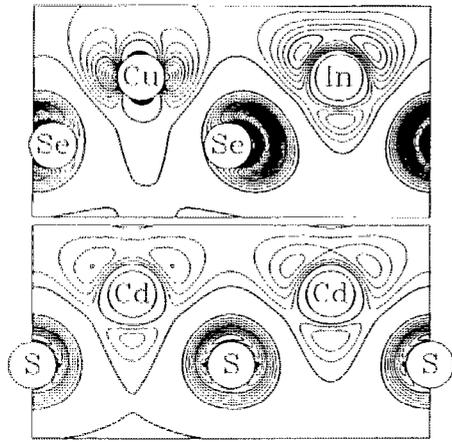


FIG. 3. Wave function square of the CBM state at both sides of the CdS/CuInSe₂ heterojunction. Upper panel: Center layer of CuInSe₂, lower panel: Center layer of CdS.

4*p* orbital in ZnSe [i.e., the first term in Eq. (2)]. (v) The VBM wave function is strongly localized on the CuInSe₂ side with large Se *p* and Cu *d* contributions (Fig. 2).

Having established that the CBM resides on the *absorber* CuInSe₂ rather than on the window material, naturally raises the question how electron crosses the barrier into CdS in an illuminated CdS/CuInSe₂ heterojunction. Three factors can contribute here.

(i) in Fig. 3 we plot the calculated CBM wave function square on both sides of the CdS/CuInSe₂ interface. We see that the CBM is delocalized on *both* sides of the interface with significant amplitude on CdS, so no severe electron trapping occurs on CuInSe₂ even without doping or nonstoichiometry at the interface. Similar results are found for the ZnSe/CuInSe₂ heterojunction. The reason that charge delocalization occurs across the interface is that this effect is controlled by the *average* binding energy of In 5*s* and Cu 4*s* vs the binding energy of Cd 5*s*. This quantity is similar on both sides of the heterojunction.

(ii) The above argument pertains to the undoped system. In practice, in a CdS/CuInSe₂ solar cell the CdS layer is doped heavily *n* type. Nelson *et al.*¹⁰ suggested that this can raise the energy level of CuInSe₂ relative to CdS due to Fermi surface pinning, hence lead to strong band bending

in the CuInSe₂ part. This will form a metallic 2D electron gas at the interface, and further help the electron-hole separation.

(iii) Recent studies¹⁸ have suggested that the real *p-n* heterojunction of a successful solar cell may not be the traditional *n*-CdS/*p*-CuInSe₂ heterojunction but a homo-junction between *p*-type bulk CuInSe₂ and the In-rich *n*-type defect chalcopyrite (*DC*). Using our calculated ΔE_v (CdS/CuInSe₂) and the measured¹⁸ ΔE_v (*DC*/CdS) we infer that ΔE_c (*DC*/CuInSe₂) is indeed very small (~ 0.05 eV).

In traditional numerical modeling of the performance of CdS/CuInSe₂ device³ one uses as input a $\Delta E_c < 0$ value and assumes heterojunction between *n*-CdS/*p*-CuInSe₂. Clearly, this assumption must be abandoned and the consequences on solar cell performance of the revised value need to be examined.

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