Band offsets at the CdS/CuInSe$_2$ heterojunction

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The traditional explanation for the successful electron-hole separation in CdS/CuInSe$_2$ solar [redacted] experiments of Nelson *et al.* for CdS/CuInSe$_2$ yielding $\Delta E_c=+1.08$ eV. Our first principles [redacted]

[redacted] $=1.04$ eV) and *n*-CdS window layers ($E_g=2.42$ eV) have [redacted] 15% at present.[2] Despite this rapid progress, the qualita- [redacted] 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 CuInSe$_2$ [redacted] band alignment was thought to be essential for electron [redacted] age of a solar cell[6] ($\Delta E_c=-0.08$ eV). Given the large [redacted] sured, using synchrotron-radiation photoemission, the [redacted] X/CdS for $X=$Si and $X=$Ge.[9] By using the transitivity [redacted] $=1.56$ eV,[7] amended later[8] to $\Delta E_c=-0.03$ and $\Delta E_v=1.41$ eV,[8] both in qualitative agreement with the paradigm [redacted] $=0.30$ eV). This unexpected result places the CBM of [redacted] a type-I band alignment which invalidates the traditional view[3,6-8] on electron transport in this system.

Uncertainties[11] regarding the stoichiometry of the deposited CdS film and the mechanical integrity of the CdS/CuInSe$_2$ interface lead us earlier[12] 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/CuInSe$_2$ system.[12] Both the calculations and the measurements were done using the same ingredients, namely finding the core [redacted] (C) level to VBM separation in (i) the pure chalcopyrite $\Delta E^{ABX_2}_{\mathrm{VBM},C}=E^{ABX_2}_{\mathrm{VBM}}-E^{ABX_2}_C$, in (ii) the pure II-VI partner [redacted] $\Delta E^{DY}_{\mathrm{VBM},C}=E^{DY}_{\mathrm{VBM}}-E^{DY}_C$, and obtaining (iii) the difference [redacted] interface. Combining these three steps gives

[redacted]

The three terms of Eq. (1) were calculated using the local density formalism, as implemented by the highly precise [redacted] dicted (Fig. 1) $\Delta E_v(\mathrm{ZnSe/CuInSe_2})=0.70\pm0.05$ eV for the relaxed interface (thus invalidating the common anion [redacted] $=1.07\pm0.05$ eV for the relaxed interface, leading to $\Delta E_c=0.31\pm0.05$ eV (Fig. 1). This should be compared to the [redacted] experimental results of Nelson *et al.*[13] $\Delta E_v=0.30$ and $\Delta E_c=1.08$ eV. While both theory and experiment agree that [redacted] $\Delta E_c>0$ (hence, a type-I band alignment) in defiance of the traditional expectation,[3,6-8] the large quantitative discrep- [redacted] *perimental* results for CdS/CuInSe$_2$. Recently, Niles and co-workers[14] responded to this challenge and performed [redacted]

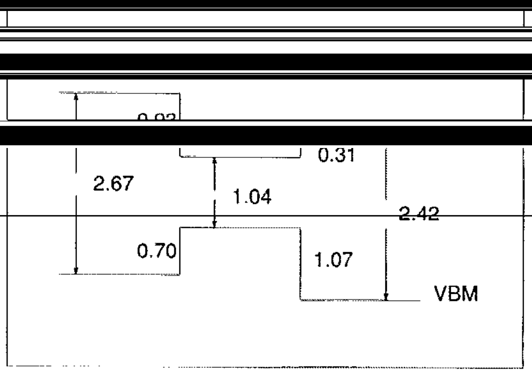


FIG. 1. [redacted] CdS/CuInSe$_2$ heterojunctions. Energies are in eV.

[redacted]

careful synchrotron-radiation measurements on high qual- [redacted] and $\Delta E_c=0.5\pm0.2$ eV, in good agreement with the theoretical predictions. Both experiment and theory then imply [redacted] port[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 [redacted] strain dependence of ΔE_v, and (iv) show that the VBM wave function is localized on the $CuInSe_2$ side while the [redacted] performing three self-consistent and fully relativistic (i.e., [redacted] culations for CdS, $CuInSe_2$, and the superstructure [redacted] culation were performed both for relaxed (incoherent) interfaces and for strained interfaces. Using in Eq. (1) the [redacted] *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 [redacted] creasing ΔE_c by 0.03 eV. For $ZnSe/CuInSe_2$ we find that coherence with $CuInSe_2$ substrate (i.e., 2% expansion of ZnSe) moves the VBM of ZnSe up by 0.10 eV while the [redacted]

To understand the physical cause and chemical trends in the valence-band offsets in these systems, consider first the common-anion case of $ZnSe/CuInSe_2$ for which the calculated and measured ΔE_v value[12] 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 [redacted] pounds[16,17] suggest, however, mixing of *cation d* character into the VBM. This reflects the interaction between anion [redacted] ting in chalcopyrites relative to binary II-VIs.[16] Note that this repulsion increases as $(\epsilon^0_{a,p}-\epsilon^0_{c,d})$ is reduced and as the

TABLE I. Breakdown of the total valence band offset ΔE_v to pure *p* [redacted] sion term [Eq. (2)], all in eV. A denotes anion and C denotes cation.

	[redacted]	[redacted]
$E^p_2-E^p_1$	0.02	0.45
R^{p-d}_{A1-C1}	0.34	0.40
R^{p-d}_{A2-C2}	1.02	1.02
$R^{p-d}_{A2-C2}-R^{p-d}_{A1-C1}$	0.68	0.62
[redacted]	[redacted]	[redacted]

contribute to ΔE_v. The total valence-band offset between a [redacted] matched semiconductor with anion *A*2 and cation *C*2 can [redacted] interaction), and a piece due to different $p-d$ repulsions in [redacted]

$$\Delta E_v=(E^p_2-E^p_1)+(R^{p-d}_{A2-C2}-R^{p-d}_{A1-C1}). \qquad (2)$$

[redacted] entirely from $p-d$ coupling. (iv) $\Delta E_v(CdS/CuInSe_2)$ exceeds $\Delta E_v(ZnSe/CuInSe_2)$ mostly because of the larger binding energy of the S 3*p* orbital in CdS relative to the Se [redacted]

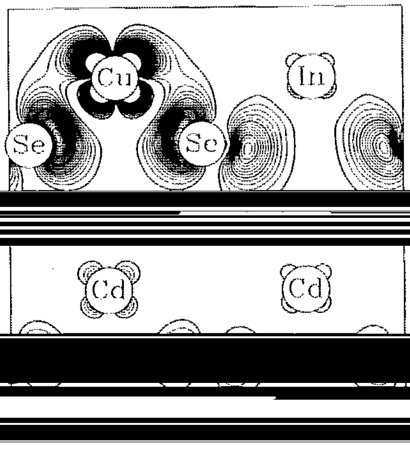
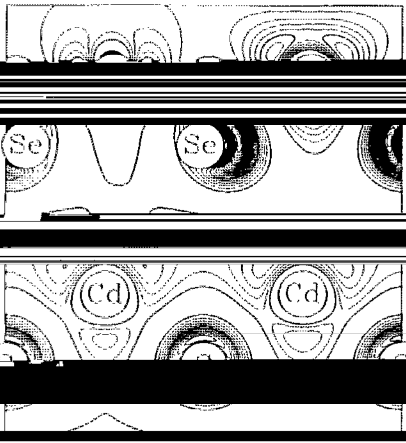


FIG. 2. Wave function square of the VBM state at both sides of the $CdS/CuInSe_2$ heterojunction. Upper panel: Center layer of $CuInSe_2$, lower panel: Center layer of CdS.



[redacted]

rally raises the question how electron crosses the barrier into CdS in an illuminated CdS/CuInSe$_2$ heterojunction. Three factors can contribute here.

(i) in Fig. 3 we plot the calculated CBM wave function square on both sides of the CdS/CuInSe$_2$ interface. We see

[redacted]

trapping occurs on CuInSe$_2$ even without doping or nonstoichiometry at the interface. Similar results are found for the ZnSe/CuInSe$_2$ heterojunction. The reason that charge delocalization occurs across the interface is that this effect

[redacted]

on both sides of the heterojunction.

(ii) The above argument pertains to the undoped sys-

[redacted]

Fermi surface pinning, hence lead to strong band bending

[redacted]

in the CuInSe$_2$ part. This will form a metallic 2D electron gas at the interface, and further help the electron-hole sep-

[redacted]

heterojunction of a successful solar cell may not be the traditional n-CdS/p-CuInSe$_2$ heterojunction but a homojunction between p-type bulk CuInSe$_2$ and the In-rich

[redacted]

we infer that $\Delta E_c(DC/\mathrm{CuInSe}_2)$ is indeed very small ($\sim$0.05 eV).

[redacted]

and assumes heterojunction between n-CdS/p-CuInSe$_2$,

[redacted]

sequences on solar cell performance of the revised value

[redacted]

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