



# Band offsets at the CdS/CuInSe<sub>2</sub> heterojunction

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The traditional explanation for the successful electron-hole separation in CdS/CuInSe<sub>2</sub> 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 on the CuInSe<sub>2</sub> absorber layer, but was sharply contradicted by the more recent photoemission experiments of Nelson *et al.* for CdS/CuInSe<sub>2</sub> yielding  $\Delta E_c = +1.08$  eV. Our first principles calculations yield for CdS/CuInSe<sub>2</sub>  $\Delta E_c = +0.31$  eV, hence, a type-I band alignment. We challenge the traditional view of the band alignment in CdS/CuInSe<sub>2</sub> heterojunctions.

Solar cells based on *p*-CuInSe<sub>2</sub> absorber layers ( $E_g = 1.04$  eV) and *n*-CdS window layers ( $E_g = 2.42$  eV) have developed rapidly from 5% efficiency in 1974 to about 15% at present.<sup>2</sup> Despite this rapid progress, the qualita-

CuInSe<sub>2</sub> remains a mystery. The band structure of CuInSe<sub>2</sub> 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<sub>2</sub>.

band alignment was thought to be essential for electron transport from CuInSe<sub>2</sub> to CdS, and to eliminate the unfavorable conduction-band spike which would have re-

$\chi$  (CuInSe)<sub>2</sub>  $\approx 4.58$  eV,<sup>5</sup> so  $\Delta E_c \approx -0.28$  eV], as well as by the zero-temperature extrapolation of the open-circuit voltage of a solar cell<sup>6</sup> ( $\Delta E_c = -0.08$  eV). Given the large uncertainties of such estimates, Turowski *et al.*<sup>7,8</sup> measured, using synchrotron-radiation photoemission, the

$\lambda$ /CdS for  $\lambda = \text{Si}^*$  and  $\lambda = \text{Ge}^*$ . By using the transitivity rule, assumed previously,<sup>2</sup> to be  $\pm 0.15$  eV, we derived that for CdS/CuInSe<sub>2</sub>  $\Delta E_c = -0.18$  eV and  $\Delta E_v = 1.56$  eV,<sup>7</sup> amended later<sup>8</sup> to  $\Delta E_c = -0.03$  and  $\Delta E_v = 1.41$  eV,<sup>8</sup> both in qualitative agreement with the paradigm  $\Delta E_c$

$= 0.30$  eV). This unexpected result places the CBM of CuInSe<sub>2</sub> above that of CdS, hence, a type-I band alignment which invalidates the traditional view<sup>3,6-8</sup> on electron transport in this system.

Uncertainties<sup>11</sup> regarding the stoichiometry of the deposited CdS film and the mechanical integrity of the CdS/CuInSe<sub>2</sub> interface lead us earlier<sup>12</sup> 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<sub>2</sub> system.<sup>12</sup> 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  $\Delta E_{\text{VBM,C}}^{\text{ABX}_2} = E_{\text{VBM}}^{\text{ABX}_2} - E_C^{\text{ABX}_2}$ , in (ii) the pure II-VI partner  $\Delta E_{\text{VBM,C}}^{\text{ABX}_2} = E_{\text{VBM}}^{\text{ABX}_2} - E_C^{\text{ABX}_2}$ , and obtaining (iii) the difference

interface. Combining these three steps gives

$$\Delta E_{\text{VBM,C}}^{\text{ABX}_2} = E_{\text{VBM}}^{\text{ABX}_2} - E_C^{\text{ABX}_2} - (E_{\text{VBM}}^{\text{ABX}_2} - E_C^{\text{ABX}_2}) + (E_{\text{VBM}}^{\text{ABX}_2} - E_C^{\text{ABX}_2}) \quad (1)$$

The three terms of Eq. (1) were calculated using the local density formalism, as implemented by the highly precise

method (Fig. 1)  $\Delta E_v(\text{ZnSe}/\text{CuInSe}_2) = 0.70 \pm 0.05$  eV for the relaxed interface (thus invalidating the common-anion rule which would have led to  $\Delta E_c \sim 0$ ). Subsequent careful

difficult case of a three-cation *two-anion* CdS/CuInSe<sub>2</sub> 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.*<sup>12</sup>  $\Delta E_v = 0.30$  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<sup>3,6-8</sup> the large quantitative discrepan-

perimental results for CdS/CuInSe<sub>2</sub>. Recently, Niles and co-workers<sup>14</sup> responded to this challenge and performed

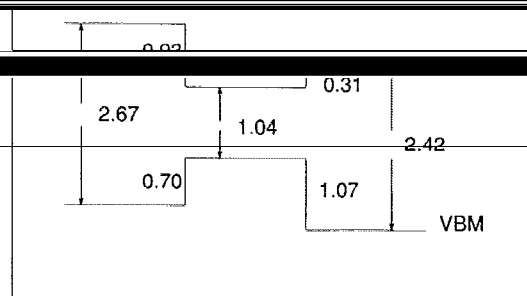


FIG. 1. Schematic of the calculated band lineup of the CdS/CuInSe<sub>2</sub> heterojunction. Energies are in eV.

careful synchrotron-radiation measurements on high quality interfaces of CdS/CuInSe<sub>2</sub>. 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

port<sup>3,6-8</sup> 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  $\Delta E$  with CuInSe<sub>2</sub> than CdS, (iii) predict the strain dependence of  $\Delta E_v$ , and (iv) show that the VBM wave function is localized on the CuInSe<sub>2</sub> side while the CBM wave function is delocalized on both heterojunction

performing three self-consistent and fully relativistic (i.e., including spin-orbit coupling) calculations for CdS, CuInSe<sub>2</sub>, and the superstructure

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  $\Delta E$  is calculated

+0.2 eV and  $\Delta E_c = 0.5 \pm 0.2$  eV, in which high quality

substrates (i.e., 1% compression of CdS). We find that the VBM and CBM of CdS

increasing  $\Delta E_c$  by 0.03 eV. For ZnSe/CuInSe<sub>2</sub> we find that coherence with CuInSe<sub>2</sub> 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/CuInSe<sub>2</sub> for which the calculated and measured  $\Delta E_v$  value<sup>12</sup> is  $\sim 0.7$  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

pounds<sup>16,17</sup> 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

gap narrowing, and to a reduction in the spin-orbit splitting in chalcopyrites relative to binary II-VIs.<sup>16</sup> 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  $\Delta E_v$  to pure *p* orbital contributions (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.

	ZnSe/CuInSe <sub>2</sub>	CdS/CuInSe <sub>2</sub>
$E_2^p - E_1^p$	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

contribute to  $\Delta E_v$ . 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* in-

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

The first term on the right of Eq. (2) is calculated for

Eq. (1) as described above. The first term on the right

state on both sides of the CdS/CuInSe<sub>2</sub> interface. We see

II-VIs since the Cu 3*d* has the smallest binding energy (small  $|\epsilon_{c,d}^0|$ ) and its orbital character is localized (small  $|\epsilon_{a,p}^0 - \epsilon_{c,d}^0|$ ), whereas the Se 4*p* orbitals are more extended and their energy is higher. (ii)  $\Delta E_v$ (CdS/CuInSe<sub>2</sub>) exceeds  $\Delta E_v$ (ZnSe/CuInSe<sub>2</sub>) mostly because of the larger binding energy of the S 3*p* orbital in CdS relative to the Se

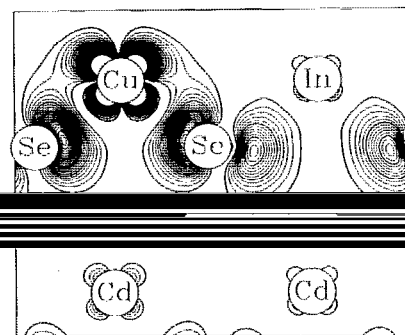
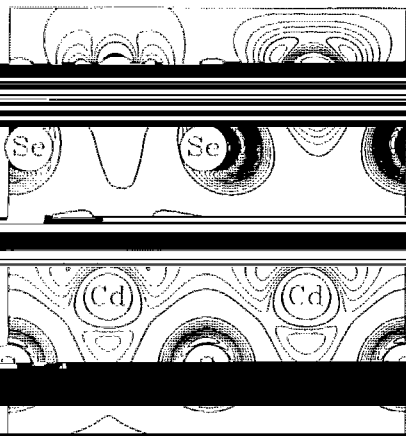


FIG. 2. Wave function square of the VBM state at both sides of the CdS/CuInSe<sub>2</sub> heterojunction. Upper panel: Center layer of CuInSe<sub>2</sub>, lower panel: Center layer of CdS.



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

heterojunction of a successful solar cell may not be the traditional  $n\text{-CdS}/p\text{-CuInSe}_2$  heterojunction but a homo-junction between  $p$ -type bulk  $\text{CuInSe}_2$  and the In-rich

$\Delta E_v(\text{CdS}/\text{CuInSe}_2)$  and the measured  $\Delta E_v(\text{DC}/\text{CdS})$  we infer that  $\Delta E_c(\text{DC}/\text{CuInSe}_2)$  is indeed very small ( $\sim 0.05$  eV).

In traditional numerical modeling of the performance and assumes heterojunction between  $n\text{-CdS}/n\text{-CuInSe}_2$ .

sequences on solar cell performance of the revised value

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FIG. 3. Wave function of the conduction band minimum (CBM) in CdS. The top panel shows the wave function in the CdS region, the middle panel shows the wave function at the CdS/CuInSe<sub>2</sub> interface, and the bottom panel shows the wave function in the CuInSe<sub>2</sub> region.

in ZnSe (i.e., the first term in Eq. (2)). (v) The CBM wave function is strongly localized on the CuInSe<sub>2</sub> side of the interface. Having established that the CBM resides on the

raises the question how electron crosses the barrier into CdS in an illuminated CdS/CuInSe<sub>2</sub> 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<sub>2</sub> interface. We see

with significant amplitude on CdS, so no severe electron trapping occurs on CuInSe<sub>2</sub> even without doping or non-stoichiometry at the interface. Similar results are found for the ZnSe/CuInSe<sub>2</sub> heterojunction. The reason that charge delocalization occurs across the interface is that this effect is controlled by the average binding energy of In 5s and Cu

on both sides of the heterojunction.

(ii) The above argument pertains to the undoped system. The energy levels of CuInSe<sub>2</sub> relative to CdS due to Fermi surface pinning, hence lead to strong band bending

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