

Band offsets at the CdS/CuInSe₂ heterojunction

Su-Huai Wei and Alex Zunger

National Renewable Energy Laboratory, Golden, Colorado 80401

(Received 7 June 1993; accepted for publication 27 August 1993)

The traditional explanation for the successful electron-hole separation in CdS/CuInSe₂ solar

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 traditional explanation for the successful electron-hole separation in CdS/CuInSe₂ 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 1974 to about 15% at present.² Despite this rapid progress, the qualitative explanation for the successful electron-hole separation in CdS/CuInSe₂ solar cells has remained elusive. The traditional explanation is 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. This band alignment was thought to be essential for electron transport from CuInSe₂ to CdS, and to eliminate the recombination of photo-generated electron-hole pairs. However, recent photoemission spectroscopy (PES) measurements by Nelson *et al.* have shown that the CBM is on CuInSe₂ and the VBM is on CdS, leading to a type-II band alignment. This result is in sharp contrast to the traditional expectation and has led to a re-evaluation of the mechanism for the successful electron-hole separation in CdS/CuInSe₂ solar cells. In this paper, we present first principles calculations of the band structure of CdS/CuInSe₂ heterojunctions. We find that the band alignment is type-I, with the CBM on CdS and the VBM on CuInSe₂. This result is in agreement with the traditional expectation and contradicts the PES measurements of Nelson *et al.* We discuss the implications of our results for the mechanism of electron-hole separation in CdS/CuInSe₂ solar cells.

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 1974 to about 15% at present.² Despite this rapid progress, the qualitative explanation for the successful electron-hole separation in CdS/CuInSe₂ solar cells has remained elusive.

The traditional explanation is 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.

This band alignment was thought to be essential for electron transport from CuInSe₂ to CdS, and to eliminate the recombination of photo-generated electron-hole pairs.

However, recent photoemission spectroscopy (PES) measurements by Nelson *et al.* have shown that the CBM is on CuInSe₂ and the VBM is on CdS, leading to a type-II band alignment. This result is in sharp contrast to the traditional expectation and has led to a re-evaluation of the mechanism for the successful electron-hole separation in CdS/CuInSe₂ solar cells. In this paper, we present first principles calculations of the band structure of CdS/CuInSe₂ heterojunctions. We find that the band alignment is type-I, with the CBM on CdS and the VBM on CuInSe₂. This result is in agreement with the traditional expectation and contradicts the PES measurements of Nelson *et al.* We discuss the implications of our results for the mechanism of electron-hole separation in CdS/CuInSe₂ solar cells.

age of a solar cell⁶ ($\Delta E_c = -0.08$ eV). Given the large uncertainty in the band offsets, it is difficult to measure, using synchrotron-radiation photoemission, the band offsets of CdS/CuInSe₂ heterojunctions. However, calculations by Nelson *et al.* for CdS/CuInSe₂ heterojunctions yielded $\Delta E_c = -0.18$ 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 $\Delta E_c = -0.30$ eV). This unexpected result places the CBM of CuInSe₂ above the band offset of CdS, leading to a type-II 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 $\Delta E_{VBM,C}^{ABX_2} = E_{VBM}^{ABX_2} - E_C^{ABX_2}$, in (ii) the pure II-VI partner $\Delta E_{VBM,C}^{ABX_2} = E_{VBM}^{ABX_2} - E_C^{ABX_2}$, and obtaining (iii) the difference

$$\Delta E_{VBM,C} = E_{VBM}^{ABX_2} - E_C^{ABX_2} - (E_{VBM}^{ABX_2} - E_C^{ABX_2}) \quad (1)$$

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

method (Fig. 1) $\Delta E_v(\text{ZnSe/CuInSe}_2) = 0.70 \pm 0.05$ eV for the relaxed interface (thus invalidating the common anion

assumption). This result is in sharp contrast to the traditional expectation and has led to a re-evaluation of the mechanism for the successful electron-hole separation in CdS/CuInSe₂ solar cells. In this paper, we present first principles calculations of the band structure of CdS/CuInSe₂ heterojunctions. We find that the band alignment is type-I, with the CBM on CdS and the VBM on CuInSe₂. This result is in agreement with the traditional expectation and contradicts the PES measurements of Nelson *et al.* We discuss the implications of our results for the mechanism of electron-hole separation in CdS/CuInSe₂ solar cells.

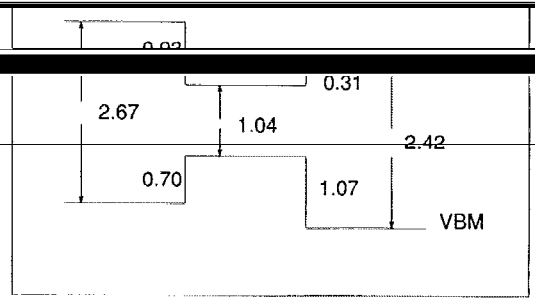


FIG. 1. Schematic of the calculated band alignment of the CdS/CuInSe₂ heterojunctions. Energies are in eV.

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

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 has a smaller ΔE 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

performing three self-consistent and fully relativistic (i.e., including spin-orbit coupling) calculations for CdS, CuInSe₂, and the superstructure (Fig. 1) (CdS) which is assumed to be 100% strained. Calculations 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 is calculated

of CdS and CuInSe₂ are $\Delta E_c(\text{CdS}) = 0.4$ eV and $\Delta E_c(\text{CuInSe}_2) = 0.2$ eV, in which high quality

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

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

pounds^{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

gap narrowing, 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 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 ₂	CdS/CuInSe ₂
$E_2^p - E_1^p$	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 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-a* interaction), and a piece due to different *p-d* repulsions 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 the *p* orbital energy difference at the VBM (in the absence of *p-a* interaction), and the second term is the difference in *p-d* repulsion between the two materials.

Eq. (2) as described above. The first term on the right of Eq. (2) is the *p* orbital energy difference at the VBM (in the absence of *p-a* interaction), and the second term is the difference in *p-d* repulsion between the two materials.

state on both sides of the CdS/CuInSe₂ interface. We see that the VBM of CdS is primarily composed of *p* orbitals, while the VBM of CuInSe₂ is primarily composed of *p* orbitals with a small admixture of *d* character. The VBM of CuInSe₂ is primarily composed of *p* orbitals with a small admixture of *d* character.

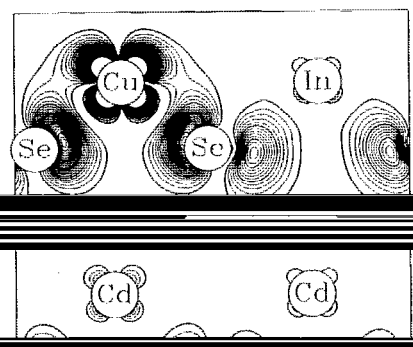
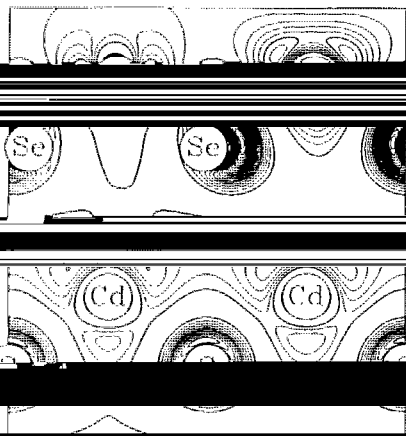


FIG. 2. Wave function square of the VBM state at both sides of the CdS/CuInSe₂ heterojunction. Upper panel: Center layer of CuInSe₂, lower panel: Center layer of CdS.



in the 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 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 (~ 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

This work was supported in part by the U.S. Department

FIG. 3. Wave function of the conduction band minimum (CBM) in CdS. The wave function is strongly localized on the CdS side of the CdS/CuInSe₂ interface, but has significant amplitude on both sides of the CdS/CuInSe₂ interface.

in ZnSe p.c., the first term in Eq. (2)]. (v) The CBM wave function is strongly localized on the CuInSe₂ side of the CdS/CuInSe₂ interface.

Having established that the CBM resides on the CdS side of the CdS/CuInSe₂ interface, we naturally raise 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 with significant amplitude on CdS, so no severe electron trapping occurs on CuInSe₂ even without doping or non-stoichiometry 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 5s and Cu 3d orbitals in ZnSe p.c., the first term in Eq. (2)]. (v) The CBM wave function is strongly localized on the CuInSe₂ side of the CdS/CuInSe₂ interface.
- (ii) The above argument pertains to the undoped sys-

¹S. Wagner, I. I. Shav, P. Migliorato, and H. M. Kasper, *Appl. Phys. Lett.* **47**, 1000 (1985).

²L. Stolt, J. Hedstrom, J. Kessler, M. Ruckh, K. O. Velthaus, and H. W.

567 (1986).

⁴R. K. Swank, *Phys. Rev.* **153**, 844 (1967).

⁵*Journal of Applied Physics*, **43**, Suppl. 1, 813 (1976).

⁶L. L. Kazmerski, J. P. Ireland, F. R. White, and R. B. Cooper, *Proceedings of the 13th IEEE Photovoltaic Specialists Conference*, Washington, DC (IEEE, New York, 1978), p. 184.

⁸M. Turowski, G. Margaritondo, M. K. Kelly, and R. D. Thomlinson, *Phys. Rev. B* **31**, 1022 (1985).

⁹A. D. Katnani and G. Margaritondo, *J. Appl. Phys.* **54**, 2522 (1983).

¹⁰A. J. Nelson, S. Gebhard, A. Rocket, E. Colavita, M. Engelhardt, and H. Hochst, *Phys. Rev. B* **42**, 7518 (1990).

¹¹A. J. Nelson (private communication).

¹²A. J. Nelson, C. B. Schroedtfager, S. H. Wei, A. Zunger, D. Dixon, D.

¹³A. J. Nelson and D. Dixon, *Phys. Rev. Lett.* **66**, 1266 (1981), and references therein.

¹⁴D. W. Niles, R. Patel, and H. Hochst (unpublished).

¹⁵D. Schmid, M. Ruckh, F. Grunwald, and H. W. Schock, *J. Appl. Phys.* **73**, 2002 (1992).