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Theoretical and experimental studies of the ZnSe/CuInSe$_2$ heterojunction band offset

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We report first-principles band structure calculations that show that ZnSe/CuInSe$_2$ has a significant valence band offset (VBO, ΔE_v): 0.70±0.05 eV for the relaxed interface and 0.60±0.05 eV for the coherent interface. These large values demonstrate the failure of the common anion rule. This is traced to a stronger Cu,*d*-Se,*p* level repulsion in CuInSe$_2$ than the Zn,*d*-Se,*p* repulsion in ZnSe. The VBO was then studied by synchrotron radiation soft x-ray photoemission spectroscopy. ZnSe overlayers were sequentially grown in steps on *n*-type [redacted] each growth in order to observe changes in the valence band electronic structure as well as changes in the In 4*d* and Zn 3*d* core lines. Results of these measurements reveal that the VBO is $\Delta E_v = 0.70 \pm 0.15$ eV, in good agreement with the first-principles prediction.

The ternary $A^{\mathrm{I}}B^{\mathrm{III}}X_2^{\mathrm{VI}}$ chalcopyrite semiconductor, CuInSe$_2$ ($E_g = 1.1$ eV), has received considerable attention as an absorber in heterojunction solar cells.[1] Technical ad- [redacted] 14%.[1] The theoretical electronic structure of CuInSe$_2$ has been calculated[2] and experimental data have confirmed the [redacted] applications as a window layer for photovoltaic heterojunctions.[4]

The ZnSe/CuInSe$_2$ heterojunction provides an inter- [redacted] ishing valence band offset. We now know[6] that this rule is violated in the above two cases involving *binary* heterojunction partners. ZnSe/CuInSe$_2$ is the first nearly lattice [redacted] heterojunction partner to be tested in this respect. This system is interesting because it involves a near-transition metal atom (copper): the failure of the common-anion rule in Zn, Cd, and Hg containing II-VI heterojunctions was attributed[6] to the different repulsion between the cation *d* orbitals and the common anion *p* orbitals on either side of [redacted] binding energy than the *d* band in Zn, Cd, and Hg-based II-VIs,[2] there is a correspondingly large difference in the *p-d* level repulsions in CuInSe$_2$ and II-VI materials. Hence, Cu-containing heterojunctions with II-VI semiconductors should exhibit a greater departure from the common-anion rule than pure II-VI heterojunctions. Progress in attaining [redacted] continuities is necessary in order to ultimately control these interfacial properties. This letter discusses theoretical [redacted] continuity and the results of a soft x-ray photoemission investigation of heterojunction formation.

We have first calculated the valence band offset (VBO) [redacted] junction partner is a ternary compound.

The band offset between two materials ABX_2 and DX [redacted]

where $\Delta E_{vbm,c}^{ABX_2} = E_{vbm}^{ABX_2} - E_c^{ABX_2}$ and $\Delta E_{vbm,c}^{DX} = E_{vbm}^{DX} - E_c^{DX}$ are the core-level (c) to the valence band maximum (vbm) [redacted] CuInSe$_2$ heterojunction in an analogous way to previous calculations on binary systems.[6] We have performed first-principles total energy and band structure calculations for the constituents CuInSe$_2$ and ZnSe, obtaining the three [redacted]

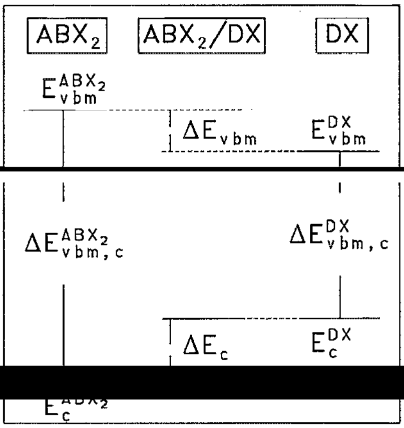

FIG. 1. Schematic energy-level diagram used to deduce the valence band [redacted]

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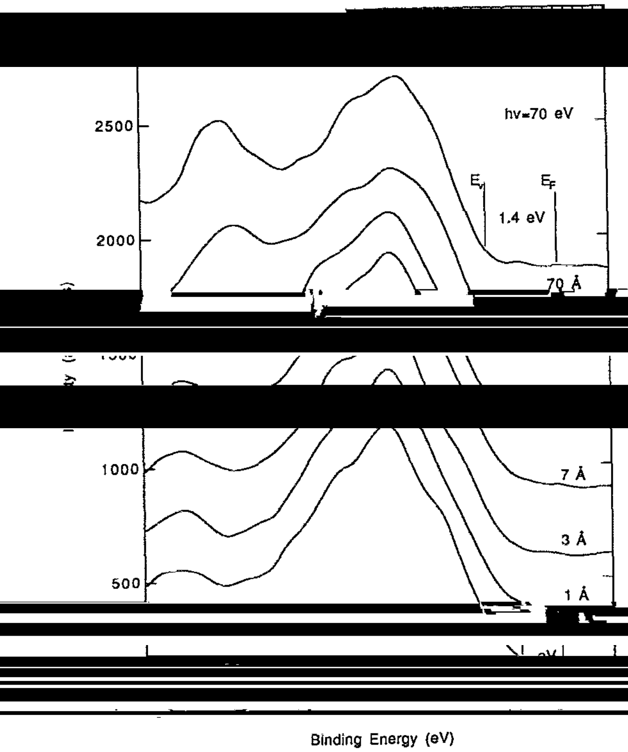

FIG. 2. Normal emission valence band spectra of the ZnSe/CuInSe$_2$ interface as a function of the effective ZnSe coverage for the *n*-type crystals. Zero of energy is at E_F.

terms of Eq. (1). The two core-to-*vbm* energy differences $\Delta E_{vbm,c}$ were obtained as eigenvalue differences in separate [redacted]

[redacted]

tices with (001) orientation. In this superlattice calculation the number of layers *p* was increased until the core energy levels of the innermost layer on each side of the interface were bulklike. We found that for $p=2$ the uncer- [redacted]

formalism[11] as implemented by the general potential, relativistic, all electron linear augmented plane wave (LAPW) [redacted]

k points for the zinc-blende zone and their equivalent **k** [redacted]

calculations. The calculated equilibrium lattice constants for CuInSe$_2$ and ZnSe are 5.736 Å (observed: 5.784 Å)[15] and 5.618 Å (observed; 5.667 Å),[16] respectively. The calculated tetragonal distortion $c/a=1.008$ and internal relaxation $u=0.214$ in CuInSe$_2$ can be compared with the observed[15] values of 1.004 and 0.224, respectively.

The calculated VBO depends on the interfacial geom- [redacted]

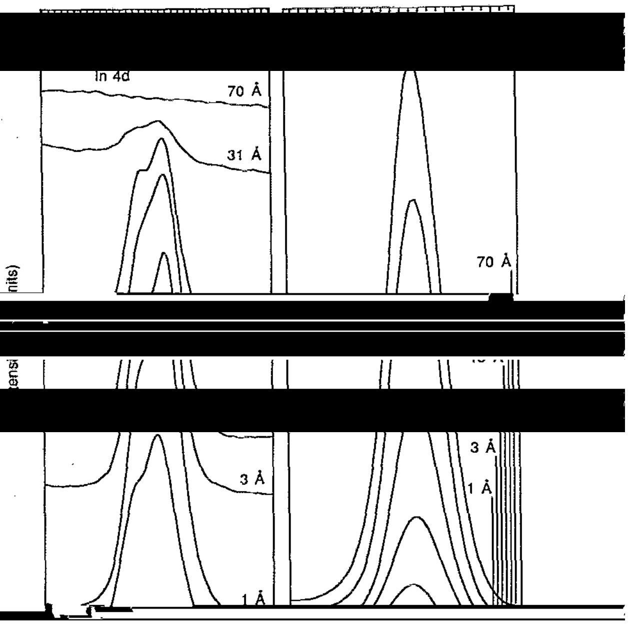

FIG. 3. Characteristic core level emission for CuInSe$_2$ as a function of the effective ZnSe coverage (a) In 4*d* and (b) Zn 3*d*. Zero of energy is at E_F.

relaxed, so each heterojunction partner attains its own equilibrium atomic geometry. This gives $\Delta E_{vbm}=0.70$ [redacted] the absence of strain, $\Delta E_{cbm}=E_g^{(1)}-E_g^{(2)}-\Delta E_{vbm}=0.90$ ±0.05 eV, where $E_g^{(1)}$ and $E_g^{(2)}$ are the bulk band gaps of [redacted]

field effect; the upper split component moves to lower binding energy by 0.1 eV, hence $\Delta E_{vbm}=0.60\pm0.05$ eV. The tensile strain in ZnSe further lowers its *cbm* by 0.1 eV, so $\Delta E_{cbm}=0.80\pm0.05$ eV. Note that in the presence of strain [redacted]

rule,[5] which states that for a common anion system the valence band offset is small. In fact, this appears to be the [redacted]

structure, the anion *p* and the cation *d* orbitals have the [redacted]

vbm to lower binding energies by an amount inversely proportional to the (metal-*d*) to (nonmetal-*p*) energy difference. In CuInSe$_2$, the Cu 3*d* orbitals have a much smaller binding energy than the Zn 3*d* orbitals in ZnSe, so the (Cu,3*d*)-(Se,4*p*) coupling in CuInSe$_2$ is much stronger than the (Zn,3*d*)-(Se,4*p*) coupling in ZnSe. This interaction pushes the *vbm* of CuInSe$_2$ up in energy relative to the [redacted] anion rule should apply. We have tested this mechanism by [redacted] considerably stronger in the ternary case.

This prediction, obtained prior to experimental testing, was tested by the photoemission measurements described next. The $CuInSe_2$ crystals were sliced from an ingot which was prepared by high-pressure liquid-encapsulated direction solidification (LEDS).[17] The samples were polished [redacted] sizes. Laue backscattering and x-ray photoemission from a single grain confirmed the (112) surface orientation and [redacted] stoichiometry. The crystal surface was sputter cleaned with 500 eV Ar ions, 30° incidence followed by annealing for [redacted] nitride effusion cell (750 °C). Photoemission spectra were [redacted] opment of the electronic structure at the heterojunction interface. These experiments were performed using the Amoco 6m torodial grating monochromator (TGM) at the University of Wisconsin Synchrotron Radiation Cen- [redacted] hemispherical sector analyzer and were measured at normal emission with $h\nu = 70$ eV and an energy resolution of $\Delta E \approx 0.1$ eV.

[redacted] tra of the $ZnSe/CuInSe_2$ interface as a function of the effective ZnSe coverage. The observed upper valence band [redacted] branches of the Cu d bands. The transition of the valence [redacted] vbm for $CuInSe_2$ and ZnSe are determined from the linear [redacted] is n-type, the cleaned $CuInSe_2$ bands are very nearly flat near the surface with minimal (<0.2 eV) band bending. [redacted] ZnSe is deposited onto the n-type $CuInSe_2$ crystal surface, the $CuInSe_2$ valence band remains flat and the structure [redacted]

The band offset can also be measured using Eq. (1). [redacted] erojunction is measured for three coverages (7, 15, and 31 Å); the average over these is 7.72 ± 0.15 eV. From Eq. (1) we have $\Delta E_{vbm} = 17.75–9.25–7.72 = 0.78 \pm 0.15$ eV, within the range given by the alternative measurement (Fig. 2) i.e., 0.6 ± 0.1 eV. Bands may bend outside this interfacial region on a length scale of ≈ 1000 Å.

[redacted] erojunction band discontinuities of $ZnSe/CuInSe_2$ and the [redacted] photoemission investigation. The theoretical model pre- [redacted] n-type $CuInSe_2$ can be constructed.

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