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Theoretical and experimental studies of the ZnSe/CuInSe₂ heterojunction band offset

Art. I. Nalepa, C. B. Schwarzberger, G. L. Hsi, W. J. and Alex Zunger

D. Rioux, R. Patel, and Hartmut Höchst

Synchrotron Radiation Center, University of Wisconsin-Madison, Stoughton, Wisconsin 53589

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We report first-principles band structure calculations that show that ZnSe/CuInSe₂ 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 CuInSe₂ 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 CuInSe₂ (112) single crystals at 200 °C. *In situ* photoemission measurements were acquired after 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 $A^I B^{III} X_2^{VI}$ chalcopyrite semiconductor, CuInSe₂ ($E_g = 1.1$ eV), has received considerable attention as an absorber in heterojunction solar cells.¹ Technical ad-
 applications as a window layer for photovoltaic heterojunc-
 tions.⁴ The ZnSe/CuInSe₂ heterojunction provides an inter-
 14%.¹ The theoretical electronic structure of CuInSe₂ has been calculated² and experimental data have confirmed the

continuity and the results of a soft x-ray photoemission investigation of heterojunction formation.

We have first calculated the valence band offset (VBO) in ZnSe/CuInSe₂, then measured it. Previous theories of
 junction partner is a ternary compound.
 The band offset between two materials ABX_2 and DX can be expressed as (see Fig. 1):
 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*) energy separations for materials ABX_2 and DX respec-

ishing valence band offset. We now know⁶ that this rule is violated in the above two cases involving *binary* heterojunction partners. ZnSe/CuInSe₂ is the first nearly lattice
 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 attributed⁶ to the different repulsion between the cation *d* orbitals and the common anion *p* orbitals on either side of the interface. Since the *d* band in Cu has a much lower 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 CuInSe₂ 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

continuities is necessary in order to ultimately control these interfacial properties. This letter discusses theoretical

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CuInSe₂ 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 CuInSe₂ and ZnSe, obtaining the three

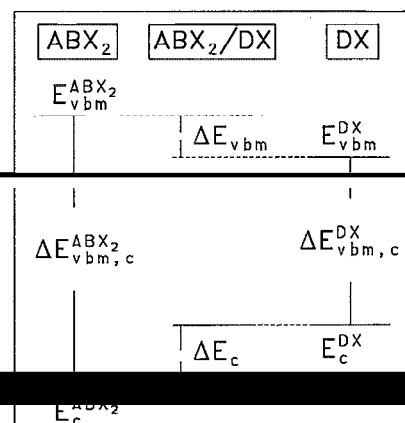


FIG. 1. Schematic energy-level diagram used to deduce the valence band offset between ABX_2 and DX .

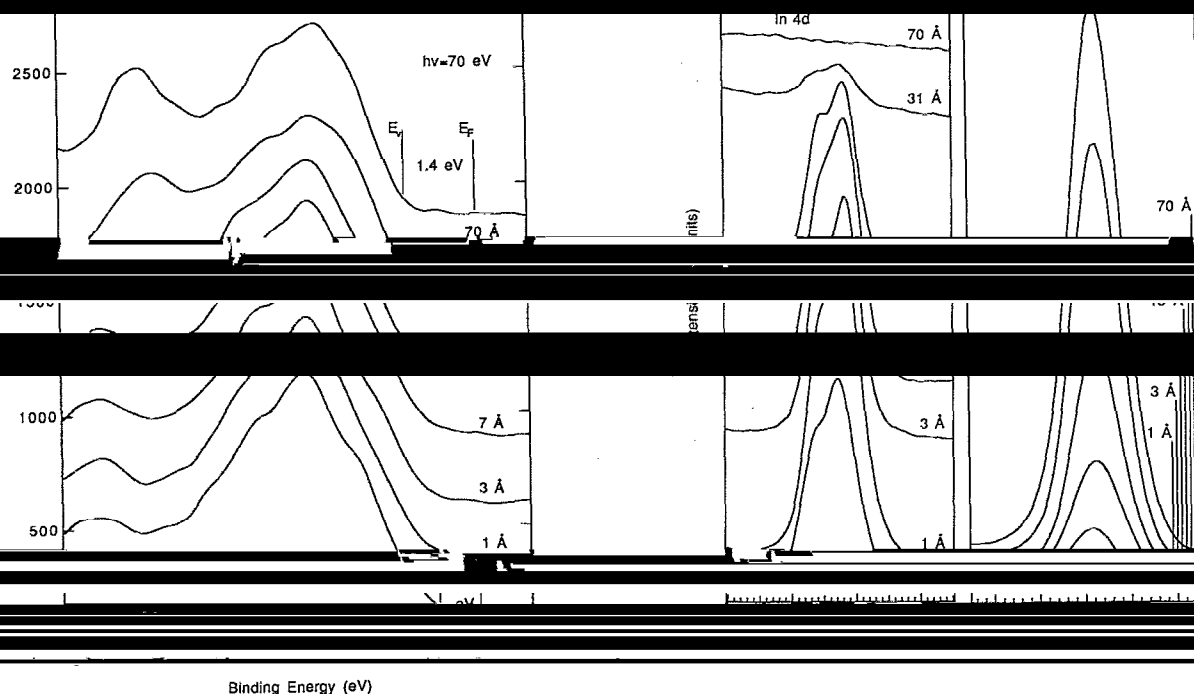


FIG. 2. Normal emission valence band spectra of the ZnSe/CuInSe₂ interface as a function of the effective ZnSe coverage for the *n*-type crystals. Zero of energy is at E_F .

terms of Eq. (1). The two core-to-*vbm* energy differences $\Delta E_{vbm,c}$ were obtained as eigenvalue differences in separate calculations on CuInSe₂ and ZnSe. The core-level difference ΔE_c between the two materials was obtained from band calculations on the (CuInSe₂)_{*p*}/(ZnSe)_{*p*} superlattices 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 uncertainty associated with using different core levels (e.g. the

formalism¹¹ as implemented by the general potential, relativistic pseudopotential augmented plane wave (GAPW) method¹² is small. The energy difference ΔE_c is determined through

Brillouin zone integrations are performed using ten special *k* points for the zinc-blende zone and their equivalent *k* points for the superlattice structures.¹⁴ The equilibrium lattice constants *a* and *c* are determined through

calculations. The calculated equilibrium lattice constants for CuInSe₂ 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 CuInSe₂ can be compared with the observed¹⁵ values of 1.004 and 0.224, respectively.

The calculated VBO depends on the interfacial geom-

FIG. 3. Characteristic core level emission for CuInSe₂ 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 $\Delta E_{vbm}=0.70 \pm 0.05$ eV with the *vbm* of CuInSe₂ above that of ZnSe. In the absence of strain, $\Delta E_{cbm}=E_g^{(1)}-E_g^{(2)}-\Delta E_{vbm}=0.90 \pm 0.05$ eV, where $E_g^{(1)}$ and $E_g^{(2)}$ are the bulk band gaps of *DX* and *ABX*₂. (ii) ZnSe is assumed to be coherently strained onto the (112) face of the CuInSe₂ substrate. In this case we find that the *vbm* of ZnSe is split by a crystal field effect; the upper split component moves to lower binding energy by 0.1 eV, hence $\Delta E_{vbm}=0.60 \pm 0.05$ eV. The tensile strain in ZnSe further lowers its *cbm* by 0.1 eV, so $\Delta E_{cbm}=0.80 \pm 0.05$ eV. Note that in the presence of strain $\Delta E_{cbm}=E_g^{(1)}-E_g^{(2)}-\Delta E_{vbm}$

are clearly in evidence. The energy difference ΔE_c is determined through the rule,⁵ which states that for a common anion system the

cation *d* orbital admixture in the *vbm*. In the zinc-blende structure, the anion *p* and the cation *d* orbitals have the same $t_2(E_{15g})$ symmetry at the zone center, hence they can

vbm to lower binding energies by an amount inversely proportional to the (metal-*d*) to (nonmetal-*p*) energy difference. In CuInSe₂, 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 CuInSe₂ is much stronger than the (Zn,3*d*)-(Se,4*p*) coupling in ZnSe. This interaction pushes the *vbm* of CuInSe₂ up in energy relative to the *vbm* of ZnSe. In the absence of this effect, the common

anion rule should apply. We have tested this mechanism by

The band offset can also be measured using Eq. (1).

considerably stronger in the ternary case.

This prediction, obtained prior to experimental testing, was tested by the photoemission measurements described next. The CuInSe₂ crystals were sliced from an ingot which was prepared by high-pressure liquid-encapsulated direc-

sizes. Laue backscattering and x-ray photoemission from a single grain confirmed the (112) surface orientation and stoichiometry. The crystal surface was sputter cleaned with 500 eV Ar ions, 30° incidence followed by annealing for ≈2 min at 500 °C to remove sputter-induced damage.

The ZnSe overlayers were deposited in steps on *n*-type CuInSe₂ at 200 °C using a liquid nitrogen shrouded boron nitride effusion cell (750 °C). Photoemission spectra were obtained after each growth in order to observe the development of the electronic structure at the heterojunction interface. These experiments were performed using the Amoco 6m toroidal grating monochromator (TGM) at the University of Wisconsin Synchrotron Radiation Center. The photoemitted electrons were analyzed using a 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.

Figure 2 shows the normal emission valence band spectra of the ZnSe/CuInSe₂ interface as a function of the effective ZnSe coverage. The observed upper valence band appears as a two peak structure corresponding to the two branches of the Cu *d* bands. The transition of the valence band maximum shows here in a direct indication of the evolution of the electronic structure leading to the ZnSe/

band for CuInSe₂ and ZnSe are determined from the linear extrapolation of the leading edge of the band.

is *n*-type, the cleaned CuInSe₂ bands are very nearly flat near the surface with minimal (<0.2 eV) band bending. No significant shift is observed in the dominant Cu *d* band

ZnSe is deposited onto the *n*-type CuInSe₂ crystal surface, the CuInSe₂ valence band remains flat and the structure becomes dominated by the uppermost ZnSe bands. However, the band offset for the clean and covered surface is $1.4-0.8=0.6$ eV.

peak positions for clean CuInSe₂ is $E_{vbm} - E_{In 4d} = 18.55 - E_F$

$E_F - 7.25$ eV. The quantity $E_{In 4d} - E_{Zn 3d}$ across the heterojunction 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

We have presented a theoretical prediction of the heterojunction band discontinuities of ZnSe/CuInSe₂ and the corroborating results of a synchrotron radiation photoemission investigation. The theoretical model predicts an offset of 0.60-0.70 eV, depending on the strain conditions and establishes *p-d* coupling as the source of failure of the common-anion rule in ZnSe/CuInSe₂. The experimentally determined valence band discontinuity for this heterojunction is 0.7 ± 0.15 eV. Based on these results, a heterojunction band diagram for ZnSe on single-crystal *n*-type CuInSe₂ can be constructed.

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- ¹A. Rockett and R. W. Birkmire, *J. Appl. Phys.* **70**, R81 (1991).
- ²J. E. Jaffe and A. Zunger, *Phys. Rev. B* **28**, 5822 (1983).
- ³A. J. Nelson, A. Rockett, E. Colavita, M. Engelhardt, and H. Hochst, *Phys. Rev. B* **42**, 7518 (1990); R. S. Crisp, D. Haneman, and J. W. Chu, *Solid State Commun.* **78**, 465 (1991).
- ⁴K. Mitchell, C. Eberspacher, J. Ermer, and D. Pier, *Proceedings of the 20th IEEE Photovoltaic Specialists Conference, Las Vegas (IEEE, New York, 1988)*, p. 1384.
- ⁵J. O. McCaldin, T. C. McGill, and C. A. Mead, *Phys. Rev. Lett.* **36**, 56 (1976).
- ⁶and J. Nelson, *J. Vac. Sci. Technol. B* **4**, 1000 (1986).
- ⁸W. E. Spicer, P. W. Chye, P. R. Skeath, C. Y. Su, and I. Lindau, *J. Vac.*

- and L. J. Sham, *ibid.* **140**, A1153 (1965).
- ¹²S.-H. Wei and H. Krakauer, *Phys. Rev. Lett.* **55**, 1200 (1985); and references therein.
- ¹³D. M. Ceperly and B. I. Alder, *Phys. Rev. Lett.* **45**, 566 (1980); J. P. L. Garbato, F. Leida, and R. Kücci, *Prog. Cryst. Growth Charact.* **15**, 1 (1987).
- ¹⁶*Landolt-Bornstein: Numerical Data and Functional Relationships in Science and Technology*, edited by O. Madelung, M. Schulz, and H. Weiss (1992).