

Chemical trends in band offsets of Zn- and Mn-based II-VI superlattices: *d*-level pinning and offset compression

Su-Huai Wei and Alex Zunger

National Renewable Energy Laboratory, Golden, Colorado 80401

-Received 15 November 1995!

Calculation of the unstrained band offsets between conventional zinc-blende II-VI superlattices -ZnS/ZnSe/ZnTe!, or between magnetic II-VI superlattices -MnS/MnSe/MnTe! or combinations thereof -MnX/ZnX! show that -i! the range of offsets spanned by different magnetic II-VI superlattices is compressed by a factor of 2 relative to the range of offsets spanned by conventional II-VI superlattices, -ii! the distance between the Mn *d* band and the valence-band maximum in MnX depends weakly on X, while in conventional II-VI superlattices -e.g., Zn 3*d* in ZnX! there is a wider spread, and -iii! unlike the case for conventional common-anion II-VI superlattices, the mixed offset DE_V -ZnX/MnX! depends strongly on X. We show that all three effects have a simple and common physical origin.

Superlattices and heterojunctions between common-cation conventional II-VI superlattices -e.g., ZnS/ZnSe/ZnTe!, be-

shifted relative to the unstrained values through the deformation potential. The change of E_{VBM} depends on the size and direction of the strain.²² We find that the total uncertainty due to the neglect of core-level deformation potential and the choice of magnetic ordering -see below! is about 0.1 eV.

The band-structure calculation is performed using the local-spin-density-functional approximation^{23,24} -LSDA! as implemented by the general-potential, *relativistic*, all-electron, linearized-augmented-plane-wave -LAPW! method.²⁵ We used the Ceperley-Alder exchange and correlation potential²³ as parametrized by Perdew and Zunger.²⁴ For MnX we assume a type-I antiferromagnetic spin arrangement. The electronic properties of type-I MnX are similar to those of the type-III ground state.²⁶

We have previously¹⁴ noted that the LSDA underestimates the spin-exchange splitting in MnX. We corrected this²⁶ via addition to the LSDA of a fitted parametric external potential, finding that this also improves considerably the agreement with experiment of many other band-structure-related properties. Here we calculate the band offset using both the standard LSDA and the LSDA-corrected -LSDA+ C ! approaches. Eight systems -ZnS/MnS, ZnSe/MnSe, ZnTe/MnTe, ZnS/ZnSe, ZnSe/ZnTe, ZnS/ZnTe, CdTe/MnTe, and MnS/MnSe! were computed directly in the present study. Our calculated unstrained valence-band offsets are given in Table I, together with our previously^{13,14} computed band offsets for ZnTe/CdTe, ZnTe/HgTe, and CdTe/HgTe. We find that transitivity is well satisfied for these *unstrained*, “natural” offsets. Hence, in Table I all of the VBM energies are related to that of ZnS. The trends -i!-iii! noted in the Introduction are evident in our results.

To understand these trends, we provide in Fig. 1 a schematic diagram showing how the atomic anion p orbitals and the cation d orbitals -both shown as dashed horizontal lines! interact to produce the VBM and the occupied d^1 bands -solid horizontal lines! in the crystal. In the zinc-blende compound with T_d site symmetry both the anion p and the cation d orbitals transform -among others! as the G_{15} -or t_2 ! representation. These two equal-symmetry states can interact with each other. The interaction between the p and d states results

in a level repulsion, inversely proportional to the unperturbed energy difference $\|e_d \geq e_p\|$. The key aspect of Fig. 1 is that due to the large exchange splitting between the Mn spin-up and spin-down d orbitals, the S, Se, and Te p orbitals lie *between* the occupied Mn d^1 and unoccupied Mn d^2 levels, while the Zn d levels are systematically well *below* the anion p levels. This explains effects -i!-iii! noted in the Introduction as follows.

in MnTe is pushed down less than that in MnS, due to the weaker p - d repulsion in the former. As a result, $DE_{d^1}(\text{MnX})$ is only weakly dependent on X .

Strong anion dependence in $DE_V(\text{ZnX/MnX})$: The band offset $DE_V\text{-ZnS/MnS}$ is 0, since the S $3p$ to Mn d^1 coupling is very strong due to the closeness of the respective energy levels. On the other hand, $DE_V\text{-ZnTe/MnTe}$ is 0, because the VBM of ZnTe is pushed up by the p - d repulsion, while in MnTe the net shift of VBM due to the p - d repulsion is very small, since the Te p orbital energy is almost in the middle between Mn d^1 and d^2 .

The hybridization of d orbitals at VBM of zinc-blende compounds reduces the spin-orbit splitting D_0 .^{13,14} In MnX, the d orbital mixing at the VBM is large -due to the small anion p to cation d energy difference!, thus the reduction of D_0 in MnX is much larger than in ZnX -Table I!. This reduction of D_0 -MnX! also reduces the upwards shift of VBM in MnX, thus enhancing effects -i!-iii! above. This spin-orbit contribution to -i!-iii! is maximal for X=Te, and smaller for X=S.

The trends discussed above are general for all II-VI superlattices and can thus be used to estimate the band offset between other related systems. For example, we expect that the band offset $DE_V\text{-MgTe/MnTe}$ should be small and positive. This is because the VBM shift due to p - d repulsion is very small in MnTe -effect -i!#, while the downward shift of the VBM in zinc-blende MgTe by the unoccupied, high-energy Mg d orbital²⁷ is compensated by its larger spin-orbit splitting - D_0 0.83 eV! relative to MnTe. This expectation is confirmed by our calculated value of $DE_V\text{-MgTe/MnTe}$ 0.17 eV, and is consistent with experimental observations,^{9,10,28} $DE_V\text{-MgTe/MnTe}$ > 0.

Our calculated band offsets given in Table I are in good agreement with a number of recent experimental measurements.³⁻¹⁰ For example, our calculated band offset $DE_V\text{-ZnSe/MnSe}$ 0.22 0.1 eV -Table I! is consistent with the measured³⁻⁷ values of $DE_V\text{-ZnSe/MnSe}$ 0.15 0.1 eV. Our calculated band offset¹⁴ of $DE_V\text{-CdTe/MnTe}$ 0.44 0.1 eV -Table I! is also in good agreement with recently measured⁸⁻¹⁰ values of $DE_V\text{-CdTe/MnTe}$ 0.48 0.1 eV using photoluminescence excitation spectroscopy. However, both the calculated

and measured results do not agree with previous prediction¹⁷ based on the dielectric-midgap model, suggesting that the VBM of MnTe lies above that of CdTe @i.e., $DE_V\text{-CdTe/MnTe}$ 1 0.6 eV#.

- ¹²L. Wang, S. Sivananthan, R. Sporken, and R. Caudano -private communication!
- ¹³S.-H. Wei and A. Zunger, Phys. Rev. B **37**, 8958 -1988!; J. Vac. Sci. Technol. A **6**, 2597 -1988!.
- ¹⁴S.-H. Wei, in *II-VI Semiconductor Compounds* -Ref. 2!, p. 71. In this paper, the band offset DE_V -MnTe/CdTe!520.3860.1 eV was calculated using standard LSDA and averaged over spin-up and spin-down ferromagnetic states.
- ¹⁵S.-H. Wei and A. Zunger, J. Appl. Phys. **78**, 3846 -1995!.
- ¹⁶J. Tersoff, Phys. Rev. Lett. **56**, 2755 -1986!.
- ¹⁷N. E. Christensen, I. Gorczyca, O. B. Christensen, U. Schmid, and M. Cardona, J. Cryst. Growth **101**, 318 -1990!.
- ¹⁸S. B. Zhang, S.-H. Wei, and A. Zunger, Phys. Rev. B **52**, 13 975 -1996!.
- ¹⁹E. Yu and T. McGill, in *Solid State Physics*, edited by H. Ehrenreich and D. Turnbull -Academic, Boston, 1992!, Vol. 46, p. 1.
- ²⁰T. M. Duc, C. Hsu, and J. P. Faurie, Phys. Rev. Lett. **58**, 1127 -1987!.
- ²¹A. Franceschetti, S.-H. Wei, and A. Zunger, Phys. Rev. B **50**, 17 797 -1994!.
- ²²F. H. Pollak and M. Cardona, Phys. Rev. **172**, 816 -1968!.
- ²³D. M. Ceperly and B. J. Alder, Phys. Rev. Lett. **45**, 566 -1980!.
- ²⁴J. P. Perdew and A. Zunger, Phys. Rev. B **23**, 5048 -1981!.
- ²⁵S.-H. Wei and H. Krakauer, Phys. Rev. Lett. **55**, 1200 -1985!, and references therein.
- ²⁶S.-H. Wei and A. Zunger, Phys. Rev. B **48**, 6111 -1993!.
- ²⁷Interestingly, the existence of a valence-band offset between the common-anion lattice-matched AlAs/GaAs pair is also ascribed @S.-H. Wei and A. Zunger, Phys. Rev. Lett. **59**, 144 -1987!# to an imbalance between difference p - d repulsions: the -empty! Al d orbital pushes the VBM of AlAs *down* while the -occupied! Ga d pushes the VBM of GaAs -a bit! *up*.
- ²⁸B. Kuhn-Heinrich, W. Ossau, H. Heinke, F. Fischer, T. Litz, A. Wang, and G. Landwehr, Appl. Phys. Lett. **63**, 2932 -1993!.