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# Band offsets and stability of BeTe/ZnSe (100) heterojunctions

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We present *ab initio* studies of band offsets, formation energy, and stability of (100) heterojunctions between (Zn,Be)(Se,Te) zinc-blende compounds, and in particular of the lattice-matched BeTe/ZnSe interface. Equal band offsets are found at Be/Se and Zn/Te abrupt interfaces, as well as at mixed interfaces, in agreement with the established understanding of band offsets at isovalent heterojunctions. Thermodynamical arguments suggest that islands of non-nominal composition may form at the interface, causing offset variations over $\sim 0.8$ eV depending on growth conditions. Our findings reconcile recent experiments on BeTe/ZnSe with the accepted theoretical description.

On the basis of experiments as well as theory, it is commonly accepted that at isovalent semiconductor interfaces the band offset is almost independent of the local atomic arrangement, except in the presence of heterovalent interlayers or antisites.[1,2] This result was originally established for the common-ion systems, and later generalized to the whole class of isovalent heterojunctions. Investigations on no-common-ion systems such as InP/GaInAs and InAs/GaSb confirmed that the band offset is independent on the atomic-scale interface arrangement, despite the different interface composition and local strain.[3–5] Remarkably, these findings have found a rationale within the linear-response theory (LRT) of band offsets,[2,6] which also accounts for the composition-dependent local strain effects.[7]

Only at heterovalent junctions does the band offset depend crucially on interface morphology, due to the different chemical valence of the atomic constituents, and it is fully explained within LRT. So far, the maximum variation experimentally detected amounts to 0.6 eV, and it was observed at ZnSe/GaAs (100).[8]

Controversial findings have been reported for the isovalent lattice-matched BeTe/ZnSe (100) interfaces. In a first paper,[9] a valence-band offset (VBO) of 0.9 eV was deduced from the luminescence spectra of BeTe/ZnSe quantum wells. In a subsequent work,[10] thin BeTe films grown on ZnSe (100) were investigated by x-ray photoemission spectroscopy. Unexpectedly, two widely different values, 0.46 eV and 1.26 eV, were measured in different growth conditions, and interpreted as due to Se- and Zn-terminated substrates.

Should this interpretation be confirmed, this result would be (a) the first case of morphology-dependent band offset at isovalent interfaces; (b) the largest VBO variation (0.8 eV) ever observed at semiconductor heterojunctions; (c) a clear violation of the LRT of offsets.

To help the interpretation of the experimental data, here we investigate the band alignment and the thermodynamical stability of BeTe/ZnSe(100), and other related junctions among (Zn,Be)(Se,Te) compounds, using first-principles density-functional-theory calculations. These have proven to be a highly reliable tool in predicting offsets at semiconductor-semiconductor interfaces.

Pseudopotential plane-wave calculations are performed using the VASP code,[11] with ultrasoft pseudopotentials[12] for Be and Zn (including Zn $3d$ states in the valence). The generalized gradient approximation [GGA-PW91 (Ref. 13)] to the exchange-correlation functional is used. All relevant properties of the binary (Zn,Be)(Se,Te) compounds are converged at a cutoff of 23 Ry. As shown in Table I, the experimental lattice parameters are reproduced within 1%. The abrupt interfaces were modeled in periodic boundary conditions by 24-atom slab supercells. For mixed or reconstructed interfaces, 48-atom supercells with a total of 24 atomic layers and 2 atoms per layer were used. Brillouin-zone integration was performed on a $6\times6\times2$ Monkhorst-Pack mesh. The in-plane (substrate) lattice parameter in the supercell calculation was chosen to be $a_{\rm sub}=5.697$ Å, i.e., the average of the theoretical bulk lattice parameters of BeTe and ZnSe.

For each interface, the supercell structure was fully optimized. This is mandatory to obtain realistic results, since Zn-Te (Be-Se) bond lengths differ by about $\pm 10\%$ from those of bulk BeTe and ZnSe. We relax ionic positions and cell parameters until forces below 0.05 eV/Å and stress along the (100) direction lower than 0.5 Kbar are obtained. The VBO is then computed following the approach described in Ref. 2. The comparison of the VBO calculated for the ideal unrelaxed and for the optimized structure confirms the importance of structural optimization, whose effects on VBO amount to about 0.4 eV.

Two kinds of abrupt interfaces are possible at BeTe/ZnSe(100) heterojunctions: the Zn/Te interface, characterized by the sequence of atomic planes ...-Be-Te-Be-**Te**-**Zn**-Se-Zn-Se-... , and the complementary Be/Se interface, with the stacking sequence ...-Te-Be-Te-**Be**-**Se**-Zn-Se-Zn-... . In supercells with periodic boundary conditions, interfaces are always present in pairs, and they may be cho-

TABLE I. Theoretical and experimental (Ref. 19) lattice parameters (in Å) of the zinc-blende compounds considered in this work.

| Compound | BeTe | BeSe | ZnSe | ZnTe |
|---|---|---|---|---|
| Expt | 5.626 | 5.139 | 5.668 | 6.104 |
| GGA-PW91 | 5.661 | 5.174 | 5.734 | 6.182 |

TABLE II. Valence-band offset (in eV) at different BeTe/ZnSe interfaces. The valence-band top edge is higher in BeTe than in ZnSe.

| | (100) abrupt | | | (100) $c(2\times2)$ | | (110) |
|---|---|---|---|---|---|---|
| Structure | Zn/Te | Be/Se | Asym | Zn-Be | Se-Te | Abrupt |
| Ideal | 0.16 | 0.13 | 0.15 | 0.12 | 0.12 | 0.14 |
| Relaxed | 0.54 | 0.51 | 0.51 | 0.53 | 0.52 | 0.59 |

sen (for the present orientation) to be different or identical, depending on the atomic filling of the supercell. We consider supercells both with identical, symmetry-equivalent interfaces (the first two columns of Table II) and asymmetric supercells with different interfaces (the third column of the Table, marked ''asym''). The comparison of the results allows to reduce the numerical uncertainty in the estimate of the VBO. Supercells with symmetry-equivalent interfaces exhibit a nonideal $c/a$ ratio due to local strain in the interface regions, whereas in supercells with different and complementary interfaces the local positive and negative strains nearly compensate, and $c/a$ is close to the ideal unstrained value. The average VBO for the abrupt relaxed (100) interfaces is 0.52 eV, and all values fall within a range of $\sim$30 meV, which is of the order of magnitude of the numerical uncertainty of the calculations ($\sim$10 meV), in analogy to the results for other no-common ion heterojunctions.[3–5] The equivalence of the two interfaces occurs also for the ideal unrelaxed cases. Therefore, LRT is valid also for this system, despite the large chemical differences between the constituting compounds (e.g., BeTe and ZnSe bulks have a very different ionicity, 0.34 and 0.59 on the Garcia-Cohen scale[14]). The validity of LRT is also confirmed by the fact that, for the unrelaxed case, the VBO for the abrupt (110) interface is close to the average of the two different (100) terminations. The VBO's between differently oriented, relaxed interfaces shows larger differences; but this is not in contrast with the LRT picture, because local interface strains depend not only on composition but also on orientation. From all the above results, we definitely rule out the possibility that the difference of about 800 meV between the VBO's measured at BeTe/ZnSe (100) interfaces can be simply ascribed to chemically different abrupt interfaces.[10]

As a further check, we studied some prototypical (100) nonabrupt interfaces, restricting to either anion- or cation-intermixed cases (antisites are generally energetically unfavorable in II-VI compounds). In particular we consider $c(2\times2)$ reconstructed interfaces with one mixed layer of either Be and Zn atoms (fourth column in Table II) or Se and Te atoms (fifth column in the Table). Again, the VBO is independent of the interface local atomic arrangement within 10 meV. Therefore, we conclude that the VBO at BeTe/ZnSe (100) heterojunction does not depend on the interface local atomic arrangement, thus confirming previous evidence for isovalent interfaces, and the general predictions of LRT.

Our density functional theory (DFT)-GGA VBO values are not directly comparable with experimental data, since spin-orbit coupling and self-energy effects on bulk bands are not taken into account in the present electronic structure calculations. The spin-orbit splitting is 0.96 eV for BeTe and 0.40 eV for ZnSe; including *a posteriori* the ensuing correction to the VBO reported in Table II, we obtain an estimate of about 0.7 eV. Many-body corrections to valence-band top edges, still excluded from this estimate, are not available for these compounds to our knowledge. Typical values for these corrections are of order 0.1–0.2 eV,[16] so that a final theoretical estimate could be close to the experimental value of 0.9 eV reported in Ref. 9 and, incidentally, to the average of the two values of Ref. 10. However, we stress that the corrections to the DFT-GGA VBO values are bulk quantities, and thus they affect the *absolute* value of the VBO, but not at all the *relative* comparison among the values for different cases considered here. Therefore, the main result of our calculations, i.e., the independence of the VBO on interface composition, is fully valid.

According to our calculations, the VBO of 0.9 eV reported in Ref. 9 could correspond to several possible interface compositions, including either Zn/Te or Be/Se abrupt terminations or mixed interfaces. However, some suggestions about the actual structure of the interface comes from a thermodynamic investigation of interface stability. We find that in thermodynamic equilibrium *abrupt interfaces of either kind are favored over the intermixed ones*. We define the interface formation energy per unit of sectional area in the most general case as

$$2\,E_{\rm form}^{\rm intf}=E_{\rm tot}^{\rm intf}-N_{\rm Be}\mu^{\rm Be}-N_{\rm Zn}\mu^{\rm Zn}-N_{\rm Te}\mu^{\rm Te}-N_{\rm Se}\mu^{\rm Se},$$

where $E_{\rm tot}^{\rm intf}$ is the total energy of the supercell describing the interface, and the $\mu$'s and $N$'s are the chemical potentials and number of atoms of the various elements involved. At equilibrium the chemical potentials of the elements and total energies of the condensed phases are related by

$$\mu^{\rm BeTe}=\mu^{\rm Be}+\mu^{\rm Te};\qquad \mu^{\rm ZnSe}=\mu^{\rm Zn}+\mu^{\rm Se}. \tag{1}$$

The formation energy of abrupt interfaces is easily seen to be a function of the difference between Zn (or Se) and Be (or Te) chemical potentials. Indeed, using Eqs. (1), the formation energy for abrupt Zn/Te and Be/Se interfaces reads

$$2\,E_{\rm form}^{\rm Zn/Te}=E_{\rm tot}^{\rm Zn/Te}-N_{\rm Te}\mu^{\rm BeTe}-N_{\rm Se}\mu^{\rm ZnSe}-(\mu^{\rm Zn}-\mu^{\rm Be}),$$

$$2\,E_{\rm form}^{\rm Be/Se}=E_{\rm tot}^{\rm Be/Se}-N_{\rm Te}\mu^{\rm BeTe}-N_{\rm Se}\mu^{\rm ZnSe}+(\mu^{\rm Zn}-\mu^{\rm Be}),$$

respectively. The range of variation of $\mu^{\rm Zn}-\mu^{\rm Be}$ is

$$\mu^{\rm Zn}-\mu^{\rm Be}\leqslant\mu^{\rm Zn-bulk}-\mu^{\rm Be-bulk}-\Delta H^{\rm BeTe},$$

$$\mu^{\rm Zn}-\mu^{\rm Be}\geqslant\mu^{\rm Zn-bulk}-\mu^{\rm Be-bulk}+\Delta H^{\rm ZnSe},$$

where $\Delta H^{\rm X}$ is the formation entalpy for compound $X$. Mixed-interface supercells are instead stoichiometric ($N_{\rm Se}=N_{\rm Zn}=N_{\rm ZnSe}$, and $N_{\rm Te}=N_{\rm Be}=N_{\rm BeTe}$), therefore the formation energy is independent of the chemical potentials. The previous expression becomes

$$2\,E_{\rm form}^{\rm mixed}=E_{\rm tot}^{\rm mixed}-N_{\rm BeTe}\mu^{\rm BeTe}-N_{\rm ZnSe}\mu^{\rm ZnSe},$$

where now $N$'s and $\mu$'s are referred to the bulk formula unit. The results, summarized in Fig. 1, show that the Zn/Te abrupt interface is favored in high ($\mu^{\rm Zn}-\mu^{\rm Be}$) conditions, and conversely the Be/Se abrupt interface is favored in low ($\mu^{\rm Zn}-\mu^{\rm Be}$) conditions. Most interestingly we find that, unlike the case of heterovalent junctions, the present isovalent

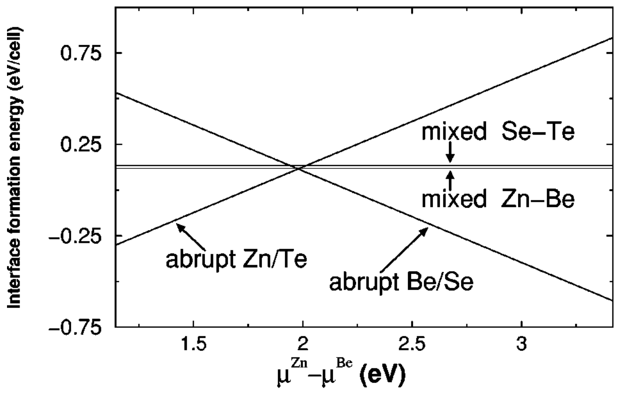

FIG. 1. Formation energy [in eV/$(1\times1)$ cell] of the abrupt and $c(2\times2)$-reconstructed BeTe/ZnSe (100) interfaces as function of the difference of the Zn and Be chemical potentials.

abrupt interfaces are always favored over the mixed ones for the whole range of admissible chemical potentials. This behavior was already predicted for the III-V isovalent GaInP/GaAs interface,[15] so we suggest that this preference for abrupt interfaces may be generally valid for *any* isovalent heterojunction.

Thermodynamics further gives key indications (at least as far as equilibrium energetics is concerned) on the possible origin of different offsets measured in real samples in particular growth conditions. Islands of *a priori* unexpected composition, such as BeSe or ZnTe, may form during the deposition of BeTe on ZnSe: specifically one expects BeSe islands in Be-rich and Se-rich growth conditions, and ZnTe islands in Zn-rich and Te-rich conditions. In terms of band offsets, the idea is that these ''heteroislands'' may in fact be the material effectively interfaced to ZnSe, and therefore largely determine the observed band offset.

The idea of islands formation is suggested by previous experience with dopant incorporation in semiconductors. It was shown theoretically[17] that rising the chemical potential of the Li acceptor up to its bulk value, Li incorporation in ZnSe is preempted by the formation of a $Li_2Se$ surface phase. Indeed, heavy Li doping of ZnSe layers in molecular-beam epitaxy growth[18] results in the formation of $Li_2Se$ islands on the ZnSe surface. In the present case the scenario is slightly more complex, as four chemical potentials are involved. We choose as reference the cation chemical potentials, both for convenience and because the cations are the mobile species; the phase diagram of the four-component interface system will thus be drawn in the $\{\mu^{Zn},\mu^{Be}\}$ plane. The reactions leading to the formation of an epitaxial compound on ZnSe at the expenses of BeTe are as follows: for ZnTe on ZnSe,

$$\mathrm{Zn}+\mathrm{BeTe}\Rightarrow\mathrm{Be}+\mathrm{ZnTe}, \tag{2}$$

and for BeSe on ZnSe

$$\mathrm{Be}+\mathrm{ZnSe}\Rightarrow\mathrm{Zn}+\mathrm{BeSe}. \tag{3}$$

These reactions will occur exothermically if the reaction energy $\Delta E$ is negative; the latter energy is given for reactions (2) and (3) by

$$\Delta E^{\mathrm{ZnTe}}=\mu_{\mathrm{s}}^{\mathrm{ZnTe}}-\mu^{\mathrm{Be}}-\mu^{\mathrm{BeTe}}+\mu^{\mathrm{Zn}},$$

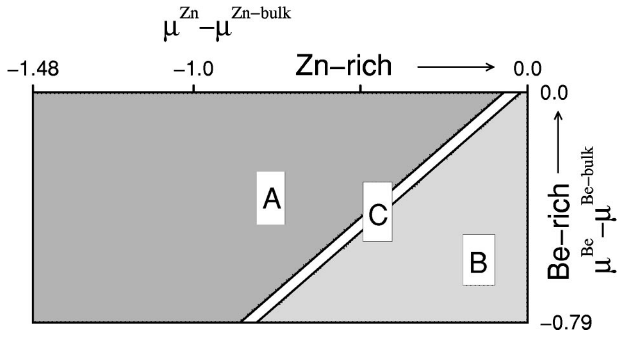

FIG. 2. Phase diagram for the (Be,Se,Zn,Te) common-ion interfaces. The stable interfaces are BeSe/ZnSe in region A, ZnTe/ZnSe in region B, BeSe/ZnTe in region C.

$$\Delta E^{\mathrm{BeSe}}=\mu_{\mathrm{s}}^{\mathrm{BeSe}}-\mu^{\mathrm{Zn}}-\mu^{\mathrm{ZnSe}}+\mu^{\mathrm{Be}},$$

respectively. In these relations, $\mu_{\mathrm{s}}^{\mathrm{XY}}$ is the total energy of bulk $XY$ in the *pseudomorphically strained* geometry on ZnSe, as it results from the optimized $XY$/ZnSe interface supercell. Using these equations and the calculated values of the chemical potentials and compounds formation energies, we determine the regions in the $\{\mu^{Zn},\mu^{Be}\}$ plane where BeTe and ZnSe are unstable with respect to trasformation into ZnTe and BeSe. The phase diagram is represented in Fig 2. In region A, $\Delta E^{\mathrm{BeSe}}$ is negative and $\Delta E^{\mathrm{ZnTe}}$ is positive: therefore the formation of epitaxial BeSe through reaction 3 is energetically favored. In region B, $\Delta E^{\mathrm{BeSe}}$ is positive and $\Delta E^{\mathrm{ZnTe}}$ negative, hence epitaxial ZnTe is energetically favored over BeTe. In region C, both the ΔE's are negative, hence both BeTe and ZnSe are unstable with respect to decomposition into BeSe and ZnTe. According to this picture, at thermodynamical equilibrium BeTe/ZnSe interfaces *are never stable* and the following interfaces may locally form instead: referring to Fig. 2, BeSe/ZnSe in region A, ZnTe/ZnSe in region B, and ZnTe/BeSe in the (very small) region C. Our present result indicates that interfaces established in real BeTe/ZnSe samples might be locally closer to ZnTe/ZnSe in Zn-rich conditions and BeSe/ZnSe in Be-rich conditions, than to the nominal BeTe/ZnSe composition. A direct consequence of this result which should be observable in experiment is the preferential formation of BeSe or ZnTe islands on ZnSe during the early stages of growth of a nominally BeTe-ZnSe interface. Our analysis does not include growth kinetics effects, which may cause the (unstable) nominally BeTe/ZnSe interface to actually form for chemical potentials in region C of Fig. 2, where the thermodynamic driving force towards equilibrium (i.e., instability of BeTe/ZnSe) is smallest.

We now discuss the key piece of information we are looking for, namely the VBO values for the various possible interfaces. In calculating them, we use the same in-plane lattice parameter $a_{\mathrm{sub}}$ as in all previous calculations (the substrate is unchanged), and carefully account for bulk and interfacial strain effects. As in the BeTe/ZnSe case, the calculated VBO values are affected by a substantial *absolute* uncertainty due to many-body and spin-orbit splitting effects, here combined with splittings coming from epitaxial strain. However, the *relative* uncertainty in comparing the values for the different systems is much smaller, due to a partial cancellation of systematic corrections to the bulk band edges.

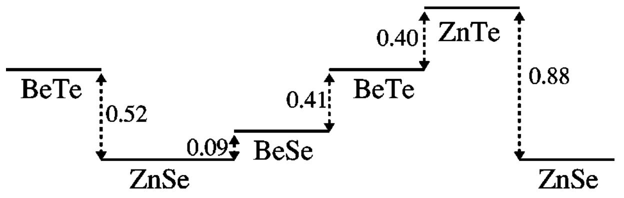

FIG. 3. Schematic of the valence-band offsets for the various interfaces investigated.

The results are depicted schematically (also including the no-common-ion lattice-matched interface) in Fig. 3. Two points are relevant in the figure: (a) the transitivity rule[2] holds within the numerical uncertainty of the calculations, confirming once again the validity of LRT for these systems; (b) the values of the VBO for the different systems differ at most by about 0.8 eV, the minimum value corresponding to the BeSe/ZnSe interface (Se-rich conditions) and the maximum to ZnTe/ZnSe (Zn-rich conditions).

It is interesting to note that the maximum calculated VBO difference of 0.8 eV is the same as the one measured in the two different samples in Ref. 10; in addition, in that experiment the maximum value was observed in Zn-rich conditions, and the minimum value in Se-rich conditions, in agreement with our findings. This matching suggest a possible correspondence between the lower (higher) experimentally measured VBO (Ref. 10) and the formation of a BeSe/ZnSe (ZnTe/ZnSe) interface, although the absolute values of the calculated offsets are about 0.3 eV lower than the measured ones, because of the discussed unaccuracy of the theoretical estimate.

In conclusion, we presented band offset calculations for a series of zinc-blende (100) interfaces between various (Zn,Be)(Se,Te) II-VI compounds. We also set up a thermodynamical phase diagram bearing on the stability of the various possible interfaces. Based on our results, we discussed recent experiments on BeTe/ZnSe interfaces, which showed a marked offset variation with growth conditions. Our conclusions are that (i) the attribution of the two widely different measured VBO values to abrupt Se-terminated and Zn-terminated interfaces of the nominal BeTe/ZnSe heterojunction, as proposed in Ref. 10, is incorrect, as well as any other attribution to mixed (reconstructed) interfaces, which have a composition-independent VBO; (ii) conversely, strained interfaces between other (Zn,Be)(Se,Te) compounds shows a VBO which may differ up to 0.8 eV in the case of BeSe/ZnSe and ZnTe/ZnSe; (iii) thermodynamics indicates that such interfaces may actually locally form in the deposition of BeSe on ZnTe and viceversa; (iv) interfaces between (Zn,Be)(Se,Te) compounds follow closely the linear reponse theory predictions just as III-V–based systems. Although the problem requires further investigation for a definite explanation, the comparison of experimental and our theoretical findings suggest that observed interfaces may locally be *not* the nominal BeTe/ZnSe, but rather interfaces such as BeSe/ZnSe or ZnTe/ZnSe depending on the chosen growth conditions.

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