Band offsets at interfaces between HgTe, CdTe, and InSb

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We have performed self-consistent density-functional calculations in order to determine the electronic structure and band offsets at ideal (110) interfaces between HgTe, CdTe, and InSb. These materials are very nearly lattice matched; strains due to the small lattice mismatch have negligible effects on the lineups. Local-density-functional theory, together with *ab initio* pseudopotentials, is used to calculate charge densities and potentials for the interface system; this allows us to determine the lineup of the bulk band structures. The following valence-band discontinuities are derived: 0.27 eV for CdTe/HgTe, 0.91 eV for HgTe/InSb, and 1.19 eV for CdTe/InSb. These values obey the transitivity rule. For HgTe/CdTe, we also examined the (100) and (111) interface orientations; the valence-band offset is the same in all cases. We have also used our simpler "model solid" approach to predict the lineups; the results are in very good agreement with those from the self-consistent interface calculations. Noticeable differences are found, however, with values obtained from model theories by Tersoff and by Harrison. Our value for HgTe/CdTe also clearly differs from $\Delta E_v \approx 0$, predicted by the common anion rule. Results for alloys can be obtained by interpolating our results for ΔE_v for the pure materials. We discuss how changing the alloy composition x in $Hg_x Cd_{1-x} Te/InSb$ interfaces can result in varying the band offsets over a wide range of values. Finally, we present a discussion of the experimental values that have been reported for HgTe/CdTe, and find good agreement between our theoretical value and the experimental result obtained from photoemission data.

I. INTRODUCTION

Heterojunctions and superlattices involving HgTe, CdTe, and InSb have received considerable experimental attention recently, because of their importance as small band-gap infrared detectors.[1] Interfaces between InSb and alloys of HgCdTe can be tuned to have a wide range of valence and conduction band offsets, depending on the composition x, as we will show in this paper. The valence-band discontinuity of HgTe/CdTe has long been thought of as being reliably given by the "common anion rule,[2]" which predicts that ΔE_v would be close to zero. This seemed to be confirmed by far-infrared magnetoabsorption measurements by Guldner et al.,[3,4] and by photoluminescence and resonant Raman scattering data by Olego et al.[5] Recent photoemission studies,[6] however, indicate that ΔE_v would be significantly different from zero, as large as 0.35 eV. Tersoff[7] was the first to point out the importance of this system as a test case for the common anion rule, and used his model, based on the lineup of charge-neutrality levels, to predict a valence-band offset of 0.51 eV. In this paper, we will report the results of full self-consistent interface calculations for these systems. Our result for CdTe/HgTe ($\Delta E_v = 0.27$ eV) will show a clear deviation from the common anion rule, but is not as large as Tersoff's prediction. It agrees well with the value derived from recent photoemission measurements.[6]

The lattice constants of HgTe, CdTe, and InSb are very similar; they are listed in Table I. We see that the mismatch between HgTe and CdTe is very small, on the order of 0.3‰. It has been suggested that strain effects might be responsible for the differences in experimentally found values for ΔE_v. A quick calculation, however, shows that the effects of strain can only lead to shifts in the valence band smaller than a few hundredths of an eV. Suppose a thin layer of HgTe is deposited on a (100) CdTe substrate, and that it is uniformly strained to match the lattice constant of the substrate. This causes an in-plane strain in HgTe: $\epsilon_\| = -0.003$. Using the theory from Ref. 8, together with the elastic constants listed in Ref. 9 and a value for the deformation potential $b(= -2/3 D_u)$ from Ref. 10, we find that the splitting of the valence-band maximum due to the uniaxial component of the strain is smaller than 0.03 eV. The shift in the valence band due to the hydrostatic contribution to the strain is typically even smaller than this. This qualitative result agrees with the calculation by Schulman et al.[11] This shows that the effect of strains on the valence-band offsets will be very small, at least compared to the discontinuity ($\Delta E_v = 0.27$ eV) that we calculate here. We have therefore taken the lat-

TABLE I. Lattice constant, spin-orbit splitting, and direct energy gap of HgTe, CdTe, and InSb (Refs. 5 and 9). Also listed are atomic configurations derived from tight-binding theory (Ref. 21) for use in model solid calculations.

a (Å)	Δ_0 (eV)	$E_g (\Gamma_6 - \Gamma_8)$ (eV)	Atomic configurations
HgTe 6.461	1.05	−0.30	Hg: $s^{1.38}p^{0.62}$; Te: $s^{1.79}p^{4.21}$
CdTe 6.481	0.93	1.59	Cd: $s^{1.27}p^{0.73}$; Te: $s^{1.70}p^{4.30}$
InSb 6.473	0.81	0.24	In: $s^{1.38}p^{1.62}$; Sb: $s^{1.75}p^{3.25}$

tice constants of all three materials to be equal ($a = 6.48$ Å) throughout the calculations.

II. METHODS AND RESULTS

The theoretical approach which enables us to calculate the band discontinuities is the same as we have applied to a wide variety of other heterojunctions, and has been described in detail elsewhere.[8,12-14] We will only mention here that the methods are based upon local-density-functional theory[15] in the momentum-space formalism,[16] using *ab initio* nonlocal pseudopotentials.[17] The pseudopotentials for Cd, respectively, Hg, include the $4d$, respectively, $5d$ electrons, as part of the core. Special points facilitate the integration over reciprocal space,[18] and the Ceperley–Alder exchange and correlation expression[19] is used.

There are two major parts to the calculation: first, we need to know the band structure of the individual semiconductors. These band energies are referred to an average potential in the solid, which we denote by $\overline{V}$, the absolute value of which is undefined in a bulk calculation. To find out how these average potentials of the two semiconductors are positioned with respect to one another at an interface (i.e., to derive $\Delta\overline{V}$), we perform a supercell calculation in which both materials are present. That will allow us to line up the band structures of the two semiconductors, and derive the band discontinuities. The thickness of the layers in the supercell that allows us to derive a converged value for $\Delta\overline{V}$ is typically quite small; the present calculations were performed with 12 atoms (six of each material) in the supercell.

In the calculations, wave functions and potentials are expanded in plane waves up to a certain maximum kinetic energy. We found it necessary to use more plane waves in the present supercell calculations than were needed for interfaces between elemental semiconductors or III–V compounds. Together with the large size of the unit cell due to the large lattice constant of the materials considered here, this lead to large matrices to be diagonalized and consequently large computation times. Our most detailed study of convergence was performed for the CdTe/HgTe (110) interface. Five different energy cutoffs between 4 and 7 Ry were applied. At 7 Ry, this corresponded to almost 900 plane waves, close to the maximum allowed by our computational facilities. Even then, no complete convergence was reached for the potential difference $\Delta\overline{V}$. It turned out, however, that all points calculated could be described by an exponential function of the cutoff; extrapolating to an infinite cutoff lead to the final result reported here. This asymptotic value was only 0.04 eV different from the value calculated at 6 Ry.

For CdTe/HgTe, we also considered the (100) and (111) interfaces. These were studied at cutoffs up to 6 Ry. Since the values for $\Delta\overline{V}$ at similar cutoffs corresponded closely to those obtained for the (110) interface, we concluded that the extrapolated final value would also be the same. For the interfaces with InSb, we report the results of interface calculations at a cutoff of 6 Ry. The associated convergence error may lead to an uncertainty in the band lineups of up to 0.1 eV.

The bulk calculations that are necessary to derive the band structure of the individual materials were all per-

formed with an 18 Ry energy cutoff. Our density-functional calculations include scalar-relativistic effects (through the pseudopotentials); this is essential for describing the s-states correctly. However, they do not take spin-orbit splittings into account. Although these splittings are substantial for the materials that we study here, they are also quite similar; this leads us to expect that they can safely be included as a perturbation *a posteriori*. For that purpose we use experimental values for the spin-orbit splittings (listed in Table I). The calculated threefold degenerate top of the valence band will correspond to the weighted average of the valence bands $E_{v,av}$ after the splitting Δ_0 is introduced; the topmost twofold degenerate band, E_v, is at an energy $\Delta_0/3$ above the average $E_{v,av}$. The values for ΔE_v that we quote have all been adjusted to include this correction. We adopt the convention that ΔE_v (A/B) is positive when the valence band in B is higher in energy than the valence band in A.

Our values for valence-band offsets are listed in Table II. We estimate the overall accuracy of these results to be on the order of 0.1 eV. Directly derived values for conduction-band discontinuities would in general suffer from the deficiencies of the density-functional method, which does not yield the correct band gaps. It is straightforward, however, to use the present results for ΔE_v, in conjunction with experimental values of the band gaps, to derive ΔE_c. Experimental data for the (direct) energy gaps are listed in Table I. In Fig. 1, we show the band lineup picture for CdTe/HgTe resulting from our calculations.

III. DISCUSSION

An important finding of this study is that (100), (110), and (111) interfaces all gives rise to the same valence-band discontinuity. This conclusion is the same as what we found for the GaAs/AlAs interface.[12,14] We should point out that our calculations for CdTe/HgTe (111) interfaces were actually performed on a supercell which contains both a (111) and a ($\overline{1}\overline{1}\overline{1}$) interface. This is unavoidable, since each slab that forms part of the superlattice necessarily has a (111) and a ($\overline{1}\overline{1}\overline{1}$) surface. Our result for this orientation should therefore be considered an average of the actual values for the (111) and ($\overline{1}\overline{1}\overline{1}$) interfaces. We expect, however, that these values will be very similar. One argument for this is that all interfaces examined [(110), (100), and (111)] gave the same lineup results, which seems to indicate that the offsets are not sensitive to the detailed structure of the interface. Another argument is based upon inspection of the potential that we calculated for the (111) supercell. If the po-

TABLE II. Valence-band discontinuities for interfaces involving CdTe, HgTe, and InSb. We list values from the present self-consistent interface calculations (SCIC) and from our model solid approach. Also shown are values from Tersoff's theory (Ref. 7).

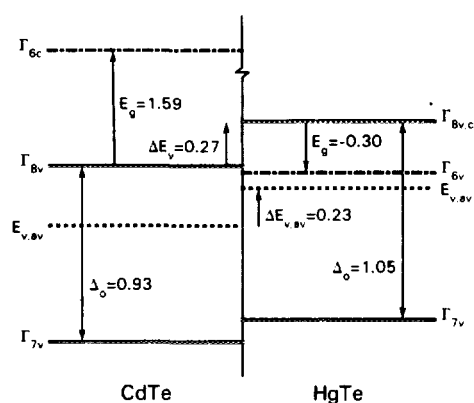| | | ΔE_v (eV) | |
	SCIC	Model solid	Tersoff
CdTe/HgTe	0.27	0.24	0.51
CdTe/InSb	1.19	1.02	0.84
HgTe/InSb	0.91	0.78	0.33

FIG. 1. Relative position of valence and conduction bands at a CdTe/HgTe interface. The discontinuity in the average valence bands, $\Delta E_{v,av}$, is obtained from self-consistent interface calculations. Spin-orbit splittings and energy gaps are taken from experiment (Table I). All energies are in eV.

tential lineup were different for the (111) and ($\overline{1}\overline{1}\overline{1}$) interfaces that are present in this cell, this would necessarily lead to the presence of an electric field in the layers. No slope in the potential was observed, however (to within 0.1 eV), indicating that the offsets for both the (111) and ($\overline{1}\overline{1}\overline{1}$) interfaces are the same.

It is relevant to examine to what extent our results for band offsets reflect linearity; this is important to assess the assumptions of linear model theories which predict lineups on the basis of bulk properties only. The results reported above for the set of interfaces CdTe/HgTe/InSb were derived from *ab initio* calculations which do not make any assumptions about linearity. We see, however, that these results obey the transitivity rule, i.e.,

$$\Delta E_v(\text{CdTe/HgTe}) + \Delta E_v(\text{HgTe/InSb})$$

$$\approx \Delta E_v(\text{CdTe/InSb}),$$

to within 0.01 eV. We have found the same result for a wide variety of other heterojunctions,[12-14] confirming the validity of the linear approach.

Our results for CdTe/InSb interfaces correspond to a type-I lineup (the InSb valence band lies above the CdTe valence band, and the InSb conduction band is lower than its counterpart in CdTe), while the values for HgTe/InSb interfaces correspond to a type-III or broken-gap lineup. It is therefore to be expected that a crossover between different types of lineups will occur as a function of alloy composition for a $\text{Hg}_x\text{Cd}_{1-x}\text{Te/InSb}$ interface. To derive results for alloys,[8] we interpolate our results for valence-band discontinuities which were derived for the pure materials. The band gap of $\text{Hg}_x\text{Cd}_{1-x}\text{Te}$ is also linear as a function of composition x;[20] linear interpolation is therefore also valid for the conduction band discontinuities. We find that with increasing Hg content (x) of the alloy, a crossover from type I to type II occurs for $x \approx 0.10$; at that point, the conduction bands in the two materials line up. Further increasing the Hg content to $x \approx 0.25$ leads to a lineup of the alloy conduction band with the InSb valence band, i.e., a crossover to a type-

III heterojunction. It should be possible to verify these theoretical predictions experimentally, by observing electron and/or hole confinement in specific regions of a superlattice constructed from these materials.

The present authors have also developed a model theory that provides reasonably accurate values for a wide variety of heterojunctions.[13,14] This approach involves the calculation of the average potential $\overline{V}$ inside each semiconductor on an absolute scale. These values can then be used to line up the band structures of two semiconductors, yielding the band offsets. This method eliminates the need for a hard and time-consuming interface calculation. The derivation of $\overline{V}$ on an absolute scale requires a choice of boundary conditions; we have found that a model for the solid which consists of a superposition of neutral-atom charge densities is particularly suited for the interface problem. Our conventions for the definition of $\overline{V}$ on an absolute scale have been described elsewhere[13,14]; for the present problem we have used the atomic configurations[21] listed in Table I. The "model solid" results for the interfaces studied here are also given in Table II. We see that for CdTe/HgTe the result is very close to that from the self-consistent interface calculation (SCIC). For the other interfaces, the results are within 0.20 eV. The model solid approach yields, by construction, the same offsets irrespective of interface orientation; for CdTe/HgTe, this result was confirmed by the self-consistent calculations.

In Table II we also list predictions for ΔE_v obtained with Tersoff's theory.[7] The main difference with our values is that Tersoff predicts an even larger valence band discontinuity in CdTe/HgTe. His value for HgTe/InSb is also significantly different from ours. Recently, Harrison has proposed a lineup scheme which is based upon the same principles of lineup of charge neutrality levels as Tersoff's approach, but implemented in a tight-binding context.[22] His results are very similar to Tersoff's.

We should also compare our values with reported experimental results. For CdTe/HgTe, extensive magnetoabsorption measurements have been performed.[3,4] The data are consistent with band structures derived from superlattice calculations (in the envelope function approximation), in which ΔE_v was set to be smaller than 0.10 eV. A similar small value was quoted as an upper limit for ΔE_v as a result of photoluminescence and Raman experiments by Olego et al.[5] The results from this group of experiments are markedly different from the value $\Delta E_v = 0.35 \pm 0.06$ eV obtained by means of x-ray photoemission spectroscopy.[6] This type of experiment provides a direct measurement of ΔE_v, in contrast with the magnetoabsorption work, which depends on an interpretation in terms of a theoretically calculated band structure for the superlattice. To our knowledge, such calculations have only been performed using small ΔE_v values; it is therefore still possible that the experimental results would also be consistent with a larger valence band discontinuity. The unusual (inverted) band structure of HgTe makes it difficult to predict positions of subbands in quantum wells or superlattices with simple arguments; the presence of a quasi-interface state[23] may also complicate experimental observations. Detailed superlattice calculations, using the presently calculated larger valence-band offset, will be necessary. For

CdTe/InSb, finally, an experimental value for ΔE_v of 0.87 ± 0.10 eV has been reported.[24] However, the interface considered in this experiment, although grown under optimum conditions used in molecular-beam epitaxy, was not abrupt.

It is clear that our value for the valence-band discontinuity at the CdTe/HgTe interface is different from the prediction of the common anion rule.[2] Two other pairs of semiconductors with a common anion have recently been examined theoretically[12,14] and experimentally, in both cases leading to valence-band offsets which clearly differ from zero. For AlSb/GaSb, our self-consistent interface calculations give $\Delta E_v = 0.38$ eV (experiment: 0.40 eV,[25] 0.45 eV[26]); for AlAs/GaAs, we find $\Delta E_v = 0.37$ eV (experiment: 0.40 eV,[26,27] 0.55 eV[28]). These instances, along with the result for HgTe/CdTe presented here, provide convincing evidence of the failure of the common anion rule.

Note added in proof: The effect of our pseudopotentials treating the outermost *d* orbitals in Cd and Hg as part of the core, thereby neglecting hybridization between these states and the top of the valence band, has been discussed by G. B. Bachelet and N. E. Christensen [Phys. Rev. B **31**, 879 (1985)], and in the context of band lineup calculations by A. Zunger (to be published). For the case of CdTe/HgTe, we estimate (on the basis of the model solid approach[14]) that *p–d* repulsion could increase the valence-band offset by up to 0.2 eV. Inclusion of this effect will, however, not alter our main conclusions regarding transitivity, orientation independence, and deviation from the common anion rule.

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