Theoretical calculations of semiconductor heterojunction discontinuities

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We have performed self-consistent density functional calculations on semiconductor heterojunctions, using *ab initio* nonlocal pseudopotentials, and have derived valence band discontinuities for many different interfaces between both lattice-matched and strained epitaxial layers. The agreement with reported experimental values is very reasonable. Based on the information obtained from the interface calculations, we have developed a new and simple approach to derive band discontinuities. In this scheme, the lineup of potentials between two materials is determined by the difference in average potentials which are calculated for a "model solid" consisting of neutral, spherical atoms. Band structures for the bulk solid are then aligned according to these average potential positions. This is a valuable ansatz which, for many cases, yields results close to those obtained from full self-consistent interface calculations. We also discuss examples, such as polar interfaces, where this simple ansatz is not sufficient.

I. INTRODUCTION

The band alignment at a semiconductor heterojunction is the single most important property for the characterization and design of novel heterostructure devices, such as quantum well lasers and high-mobility modulation-doped field-effect transistors. Recently, a lot of attention has been focused upon the determination of revised values for the GaAs/AlAs system,[1] and it is to be expected that similar efforts will be made to establish the experimental values equally well for other systems. Theoretical analysis of the problem is necessary to understand the underlying mechanism of the lineups, and to be able to predict values for new structures. The central problem is the derivation of the potential shift which occurs at the junction of two materials. In the neighborhood of the interface, the electron distribution will clearly differ from the bulk, setting up a dipole moment which will cause shifts in the bands, even far from the interface. Nevertheless, several heterojunction theories[2-4] are based only on (calculated or experimental) information about the bulk materials, without taking the actual electronic structure of the interface into account. In particular, Tersoff's theory[4] has received considerable attention recently because it produces the best results, is able to deal with both Schottky barriers and semiconductor heterojunctions in a unified fashion, and is based upon simple screening arguments. In this paper we discuss the extent to which calculations support the idea that band alignments can be found from bulk information, and we present a new simple model.

The only way to obtain a full picture of the interface problem is to carry out self-consistent calculations in which the electrons are allowed to adjust to the specific environment around the junction. Density functional theory[5] provides a fundamental theoretical framework to address this problem, and has the advantage that one can use the same methods which have been applied to a wide variety of solid state prob-

lems.[6] Calculations have been done years ago by Pickett *et al.*,[7] which followed this *ab initio* approach, except in one respect: the use of empirical pseudopotentials. In our studies, we have used the more recent *ab initio* pseudopotentials,[8] which provide a better justified starting point. We have applied the method to both lattice-matched and strained-layer[9] interfaces between pairs of elemental, III–V and II–VI semiconductors. All interfaces considered here are ideal, in the sense that the atoms occupy the positions of the bulk lattice structure up to the interface. For the strained-layer cases, strains are chosen such as to minimize the elastic energy. A description of these computations has been presented elsewhere.[10,11]

Apart from deriving explicit results for valence band offsets, we were able to draw some general conclusions from these calculations.[11] For lattice-matched, nonpolar interfaces, we noticed that the band offsets were independent of orientation, and obeyed the transitivity rule, i.e., the band offsets between two materials could be determined as the difference between the offsets of each of the materials with respect to a third. This additivity rule also applies to nonpolar, strained-layer interfaces, as was checked for the Si/Ge/GaAs system,[12] provided that the materials are kept in identical strain conditions. All this seemed to indicate the possibility of assigning a characteristic energy to each semiconductor, to which all the band energies would be referred. Band offsets would then be obtained by lining up the band structures of two materials according to these characteristic energies. In Sec. II, we will describe how we define such a value by considering a reference model solid, and illustrate the procedure with the example of the Si/Ge interface. Section III will contain a list of results, and comparisons with full interface calculations, other theories, and experiment. It is very important to recognize that this approach is only valid within the above-mentioned restrictions regarding materials and interface orientations, and that deviations will

certainly occur in other cases. Examples where the approach does not apply will also be discussed.

II. DEFINITION OF A REFERENCE MODEL SOLID

In previous work[10,11,12] we have obtained charge densities and potentials by performing full density functional calculations on a supercell which includes both materials. Such self-consistent calculations tend to be complicated and time consuming. Our goal here is to abstract essential features of these calculations, and to investigate the possibility of deriving the potential shift purely from information about the bulk materials. The lineup of the electrostatic potentials is the only part of the problem determined by the interface; all other questions are adequately treated by bulk calculations. The fundamental difficulty is that, because of the long range of the Coulomb interaction, the zero of energy is undefined for an infinite (bulk) crystal, and so there can be no reference with which to compare the potentials for two different solids. Such an absolute scale only enters into the problem when one does not deal with an infinite solid, but instead the crystal is terminated, i.e., by a surface. Unfortunately, surface calculations tend to be even harder than interface calculations. We therefore propose to derive the potential shift by using a simple representation of the bulk materials. We consider a "model solid" which will provide a reasonable description of certain properties of the material, while being significantly easier to analyze.

We construct the model solid by taking a superposition of neutral atomic spheres. The potential outside each such sphere goes exponentially to (an absolute) zero; this will be the zero of energy for the model solid. When we use such neutral, spherical objects to construct a semi-infinite solid, the presence of a surface will not induce any shift in the average potential, since no dipole layers can be set up. This feature of the model was also stressed in earlier work that used the overlapping spherical atomic charge-density approximation, for instance to calculate work functions.[13] This also means that the potential shift between two solids will only depend on "bulk" properties, and not on the specific arrangement of atoms at the interface.

One has to check, of course, that such a model solid can adequately represent the real crystal. This is not difficult to imagine in the case of elemental semiconductors like Si or Ge, but somewhat harder to understand for materials in which the bonds have more of an ionic character, such as the III–V or even the II–VI compounds. Apart from the *a posteriori* justification that the obtained results are quite good, we can also rely on information obtained from pseudopotential[14] or tight-binding[15] calculations on bulk materials. Examination of the distribution of electrons in the bonds shows that the number of electrons around each atom is approximately equal to its nuclear charge, i.e., one can still talk about "neutral spheres."

Full information about the atomic potential can be obtained by performing an atomic calculation (of the Herman–Skillman type). Since all our calculations for the solid are based on pseudopotentials, we actually perform the atomic calculations on the "pseudoatom," obtaining the potential and charge density. We now must find the average potential

in the model solid, which is a superposition of atomic charge densities. The total potential is the sum of ionic, Hartree, and exchange and correlation potentials:

$$V^l = V^{\mathrm{ion},l} + V^H + V^{xc}. \tag{1}$$

The superscript l on $V^{\mathrm{ion},l}$ reflects the fact that we are working with nonlocal pseudopotentials.[8] The choice of angular momentum component does not influence the final results, so long as we consistently use the same angular momentum component of the pseudopotential as our reference. The first two terms in Eq. (1) are linear in the charge density, and can therefore also be expressed as a superposition of atomic potentials. Their average value in the solid is

$$\overline{V}^{\mathrm{ion},l} + \overline{V}^H = \sum_i (1/\Omega) \int (V_i^{\mathrm{ion},l} + V_i^H) d\tau, \tag{2}$$

where Ω denotes the volume of the unit cell, and the index i runs over all atoms in the unit cell. Convergence is no problem in the numerical integration, since for each neutral atom the long-range part of the ionic potential (which is the same for each l) is canceled by the Hartree potential.

The exchange and correlation potential V^{xc} is not linear in the charge density, and can therefore not be expressed as a superposition of atomic potentials. This contribution, however, is local in nature and does not depend upon the specific way in which we terminate the solid. It can easily be calculated for a bulk solid, and added in afterwards. Since the local exchange and correlation potentials are proportional to $\rho^{1/3}$, we expect their average to scale with the volume as $\Omega^{-1/3}$. Tests have shown that this way of deriving the exchange and correlation contribution to the average potential reproduces the actual values, found from supercell calculations, to better than 0.02 eV.

We illustrate the procedure with the example of a Si/Ge (001) interface between cubic Si and strained Ge.[10] The lattice constant in the plane of the interface is fixed to the Si value of 5.43 Å, and the Ge side is appropriately strained to minimize the elastic energy. To perform the atomic calculations, we have to choose a configuration, i.e., the occupation x and y of the s and p orbitals: $s^x p^y$ (the d character of the bonds is small in the semiconductors that we studied here). Naturally, we want this choice to be as close as possible to the configuration that an atom would have in the solid. To obtain this type of information, we have used results from tight-binding theory[15] for Si: $s^{1.46} p^{2.54}$; and for Ge: $s^{1.44} p^{2.56}$. The average potentials derived from free-atom calculations tend to be rather sensitive to the choice of configuration. In Si, for instance, going from an sp^3 to an $s^2 p^2$ configuration shifts the average potential up by 0.82 eV. In Ge, the corresponding shift is 0.84 eV. Even though we may not be sure which configuration best represents the solid, it is to be expected that the configurations will be rather similar for the two materials on either side of the interface; this makes the *difference* in potentials far less sensitive to this choice. This issue is not so clear in the case of compound semiconductors, which may introduce a larger uncertainty in the values derived for those cases.

We then carry out the atomic calculations on the pseudo-atom in the configuration $s^x p^y$, and evaluate the integral in Eq. (2). From that equation, it also follows that the average

ionic and Hartree potentials are proportional to Ω^{-1}. Using the values of the volume of the unit cell in Si and Ge (taking the deformation due to strain into account), we can derive the average potentials, remembering that there are two identical atoms in the bulk unit cell. Choosing the $l = 1$ angular momentum component (as in Ref. 10), this leads to the following values of $(\overline{V}^{\,\text{ion},l=1} + \overline{V}^H)$: -9.02 eV for Si, and -8.30 eV for Ge. The exchange and correlation contributions to the average potentials are derived from the values $\overline{V}_{\text{Si}}^{xc} = -9.18$ eV and $\overline{V}_{\text{Ge}}^{xc} = -8.80$ eV for bulk Si at $a = 5.43$ Å and bulk Ge at $a = 5.65$ Å, respectively. We use the $\Omega^{-1/3}$ rule to scale them to the appropriate volume; this changes the value for the strained material to $\overline{V}_{\text{Ge}}^{xc} = -8.95$ eV. Finally, we add up the contributions for the individual materials, and find the shift in the total potential on either side of the interface: $\overline{V}_{\text{Ge}} - \overline{V}_{\text{Si}} = (-17.26$ eV$) - (-18.20\,\text{eV}) = 0.94\,\text{eV}$. This is to be compared with the value obtained from the full self-consistent calculations on the interface, using the supercell technique: $\Delta \overline{V} = 0.85$ eV. The agreement is very reasonable.

To get information about band discontinuities, we still have to perform the band calculations for the bulk materials, i.e., cubic Si and appropriately strained Ge. The bulk calculations were performed with a 12 Ry cutoff. Tests have shown that the choice of this cutoff is not critical for deriving the valence band lineups. We find that the valence band maximum in Si is 11.19 eV above the average potential $\overline{V}_{\text{Si}}$. In Ge, the strain along (001) splits the top of the valence band. The topmost valence band occurs at 11.08 eV, and the average energy of the three Γ'_{25} valence bands is 10.88 eV above $\overline{V}_{\text{Ge}}$. From our results above, we had $\Delta \overline{V} = 0.94$ eV. This leads to a discontinuity in the topmost valence band of 0.83 eV (upward step in going from Si to Ge). Or, if we look at the average valence band energy: $\Delta E_{v,\text{av}} = 0.63$ eV.

III. RESULTS AND DISCUSSION

In Table I we give an overview of our results for strained-layer systems. The specific strain situation is characterized

by the interface orientation, and by the parameter $a_{\parallel}$, the lattice constant in the plane of the interface ($a_{\parallel} = 5.43$ Å corresponds to an interface between cubic Si and strained Ge, $a_{\parallel} = 5.65$ Å to the other extreme: cubic Ge and strained Si). We give results for ΔE_v, the discontinuity in the tops of the valence band, and for $\Delta E_{v,\text{av}}$, the discontinuity in the weighted averages of the valence bands. Spin-orbit splitting effects were included *a posteriori* (the general trend for the systems described here is that spin-orbit effects increase all the values of the discontinuities by approximately 0.1 eV, which explains the difference with the results quoted in Ref. 10, which did not include spin-orbit splitting).

For strained-layer systems, the model solids should be strained appropriately, and shifts in the potentials will occur because of the volume change [see Eq. (2)]. From Table I, it is clear that this approach describes the qualitative and even the quantitative features of the strain effects very well. Looking at it from another angle, this also indicates that the influence on the potential shifts is mainly a consequence of the volume change. This has been confirmed by studying some deformation potential problems[16] with the model solid approach, and finding very good agreement with the full self-consistent calculations.

We have also studied a variety of lattice-matched (110) interfaces. The following configurations[15] were used in the free-atom calculations: Al, $s^{1.11}p^{1.89}$; As, $s^{1.75}p^{3.25}$; Ga, $s^{1.23}p^{1.77}$; Ge, $s^{1.44}p^{2.56}$; In, $s^{1.38}p^{1.62}$; P, $s^{1.75}p^{3.25}$; Sb, $s^{1.75}p^{3.25}$; Se, $s^{1.86}p^{4.14}$; Si, $s^{1.46}p^{2.54}$; Zn, $s^{1.02}p^{0.98}$. The results are given in Table II. The column "empirical pseudopotentials" contains values derived by performing self-consistent density functional calculations very similar to ours, but with empirical pseudopotentials.[7] We also list values obtained by means of the heterojunction theories of Harrison[3] and Tersoff.[4] Also shown in Table II are experimental data from various sources. At the present time, not all of these values are equally reliable. A striking example is that of the GaAs/AlAs interface, for which "Dingle's 85/15 Rule"[17] had become widely accepted; $\Delta E_v = 0.15 \Delta E_g$, where ΔE_g is the difference in direct band gaps. Since last year, however,

TABLE I. Heterojunction band lineups for different Si/Ge and Si/GaAs interfaces, characterized by interface orientation and $a_{\parallel}$. Results are from self-consistent interface calculations (S.C.I.C.) (Refs. 10 and 12), and from the present model solid approach. ΔE_v is the discontinuity in the top of the valence bands. $\Delta E_{v,\text{av}}$ is the discontinuity in the average energy of the valence bands at Γ. In all cases, the convention is used that a positive value for the discontinuity at a junction A/B corresponds to an upward step in going from A to B.

Orientation	$a_{\parallel}$ (Å)	ΔE_v (eV) (S.C.I.C.)	ΔE_v (eV) (model solids)	$\Delta E_{v,\text{av}}$ (eV) (S.C.I.C.)	$\Delta E_{v,\text{av}}$ (eV) (model solids)
Si/Ge					
(001)	5.43	0.84	0.93	0.54	0.63
	5.52	0.61	0.67	0.53	0.60
	5.65	0.31	0.36	0.51	0.56
(111)	5.43	0.85	0.86	0.58	0.59
	5.65	0.37	0.35	0.56	0.54
(110)	5.43	0.76	0.85	0.52	0.61
	5.65	0.22	0.26	0.50	0.54
GaAs/Si					
(110)	5.43	-0.14	-0.30	0.12	-0.04
	5.65	0.40	0.32	0.14	0.06

TABLE II. Heterojunction band lineups for lattice-matched (110) interfaces, obtained by self-consistent interface calculations (S.C.I.C.), and by the model solid approach. Other theoretical and experimental results are listed for comparison.

Heterojunction	ΔE_v (eV)					
	S.C.I.C.[a]	Model solid	Empirical pseudopotential[b]	Harrison theory[c]	Tersoff theory[d]	Experiment
AlAs/Ge	1.05	1.19		0.45	0.87	0.95[e]
GaAs/Ge	0.63	0.59	0.35	0.41	0.32	0.56[f]
AlAs/GaAs	0.37	0.60	0.25	0.04	0.55	0.45–0.56[g]
GaP/Si	0.61	0.45		0.50	0.45	0.80[h]
InAs/GaSb	0.38	0.58		0.52	0.43	0.51[i]
ZnSe/GaAs	1.59	1.48	2.0 ± 0.3	1.05	1.20	1.10[j]
ZnSe/Ge	2.17	2.07	2.0 ± 0.3	1.46	1.52	1.52[j]

[a] Reference 11; the numerical uncertainty is on the order of 0.05 eV.
[b] Reference 7.
[c] Reference 3.
[d] Reference 4.
[e] Reference 22.
[f] Reference 23.
[g] Reference 1.
[h] Reference 24.
[i] Reference 25.
[j] Reference 26.

this value has been challenged and new results now seem to indicate that more than 35% of the discontinuity is in the valence band.[1] Our model solid result is very close to the present experimental value; closer, indeed, than the self-consistent calculation.

For lattice-matched systems, the model solid approach will yield the same value for the band alignment, irrespective of the interface orientation. For GaAs/AlAs, this corresponds to what we found from the self-consistent interface calculations: (100), (110), and (111) interfaces gave the same band lineups (to within 0.02 eV[11]); this was also concluded from experiment.[18] Table II only contains results for the (110) orientation. For interfaces between a group IV element and a III–V or II–VI compound, or between compounds which do not have any elements in common, the (110) orientation is the only one which avoids charge accumulation without the need for mixing at the interface.[19] It has been shown[20] that for polar interfaces different types of mixing can lead to different dipoles at the interface, which significantly alter the band lineups. This effect can not be described by the present model solid approach, in which the neutral spheres cannot generate any net dipole across the interface, and it is clearly beyond the scope of *any* theory[2–4] which assumes the dipole to be fixed by consideration of the bulk alone.

We conclude by comparing our approach with previous theoretical work. Frensley and Kroemer[2] proposed a lineup scheme in which they chose the mean interstitial potential in the diamond or zinc blende structure as the electrostatic reference potential for each solid. These potentials were then lined up, taking a dipole shift into account, which was expressed in terms of electronegativity differences. It turned out that these dipole shifts were quite small in most cases, indicating that the "intrinsic" lineups were close to the true result. We came to the same conclusion in the present work, using a better justified value for the intrinsic potential. Although our approach has in common with Harrison's theory[3] that a reference energy level for each material is derived from atomic information, a key difference should be empha-

sized. Whereas Harrison assumed that the term values carry over from atom to solid, in our case all electronic energy levels are shifted by the superposition of atomic potentials. This choice to define the average potential of the model solid is better justified by self-consistent calculations and seems to be in better agreement with experiment. The model solid results also show agreement with the values from Tersoff's theory,[4] which is based upon quite different ideas about screening of quantum dipoles. Tersoff's arguments would clearly apply in extreme cases where metallic screening dominates (as in the obvious case of a junction between two metals, where our model solid approach would not be valid at all); but it is not certain to what extent they are valid for the semiconductor systems which we are studying here.[21] We think that the fact that our model solid results are so close to the results from full self-consistent calculations *and* to experimental values is remarkable and significant. To bring the values into complete agreement, extra dipole terms may need to be taken into account; however, these will amount to small corrections, and at this point we believe there is no simple universal theory that describes the exact screening mechanism.

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