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R. G. Dandrea, C. B. Duke, and Alex Zunger

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# Interfacial atomic structure and band offsets at semiconductor heterojunctions

R. G. Dandrea and C. B. Duke Xerox Webster Research Center, Webster, New York 14580

Alex Zunger

National Renewable Energy Laboratory, Golden, Colorado 80401

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The relationship between interfacial atomic structure and band offsets at semiconductor heterojunctions is explored through first-principles local density functional calculations. In particular, the effects of variations in interfacial geometry are analyzed for (001) interfaces between III-V/III-V materials. For the AC/BC case of a common atom, isovalent A-B intermixing in the noncommon atomic planes near the interface does not affect the band offset, even in the case of large lattice-mismatched systems. For quaternary AB/CD systems, there are two possible chemically abrupt interfaces (A-D or B-C); these can have offsets that differ by up to 80 meV. In those cases where the chemically abrupt AB/CD offset depends on the interfacial identity, intermixing leads to offset variations which are directly related to the offset difference between the chemically abrupt A-D and B-C interfaces. The differing behavior of common-atom versus noncommon-atom systems is analyzed in terms of the symmetry of the nearest-neighbor environment surrounding an atomic site of a composition change.

# I. INTRODUCTION

The development in the past two decades of precision highvacuum epitaxial growth techniques has affected a revolution in the engineering of modern electro-optic devices. One important reason for this is that such epitaxial growth techniques enable the layer-by-layer growth of heterostructures, and these have added several new dimensions to band gap engineering, including the control of quantum well (QW) widths (confinement effects) and of strain. The goal of epitaxial heterojunction growth is, in general, that of obtaining atomically abrupt interfaces. The degree to which this goal is achieved in postgrowth buried interfaces is currently a matter of debate. Thus, it is useful to pose the following question: How does the specific atomic geometry near an interface affect the band offset? The purpose of this article is to report the results of a series of local density functional "computer experiments" in order to answer this question for the case of III-V/III-V (001) heterojunctions.

The experimental determination of atomic-scale interfacial geometries, and of the relationship between these geometries and the resulting electronic structure of the heterojunction, is currently a research area of much interest.<sup>1</sup> Cathodoluminescence wavelength imaging techniques<sup>2</sup> have been interpreted to show that GaAs/AlGaAs QWs have well widths that vary by only  $\pm 1$  monolayer (ML) over lateral dimensions of 10  $\mu$ . Similarly, secondary ion mass spectra of AlAs/GaAs and GaAsP/GaAs interfaces grown by organometallic vapor phase epitaxy (OMVPE) at 700-750 °C have been interpreted as characteristic of atomically abrupt interfaces.<sup>3</sup> Other experiments suggest a slightly wider interfacial region. Recent scanning tunneling microscopy (STM) images of cleaved GaAs/AlGaAs (001) heterojunctions grown by molecular-beam epitaxy (MBE) show the interface width to be 2-4 ML.4 Also,

recent transmission electron microscopy (TEM) chemical lattice imaging experiments suggest an interfacial region in GaAs/AlGaAs 6 ML wide with Al compositions intermediate between the values far from the interface.<sup>5</sup> Evidence for significant interdiffusion has also been found at the Ge/Si interface at temperatures above 200 °C.<sup>6</sup> In the case of GeSi alloys grown on Si, Ge has been found to diffuse into the Si substrate.<sup>7</sup>

Nonideal growth processes brought about by heterovalent chemistry within interfaces such as Si/GaAs frequently lead to chemically nonabrupt heterovalent interfaces. In the case of polar [e.g., (001) or (111)] interfaces, simple electron-counting arguments explain why a chemically abrupt interface is energetically unfavorable.<sup>8</sup> The experimentally observed independence of the Ge/GaAs band offsets on interface growth orientation [i.e., polar (001) versus nonpolar (110)] indicates that the polar interfaces must reconstruct into a chemically nonabrupt (or intermixed) geometry.8 (This is explained in Sec. III.) Antiphase disorder represents another source of interface nonideality, not present in isovalent III-V/III-V systems. Evidence for nonabrupt GaAs/Si(111) interfaces comes from angle resolved photoemission experiments coupled with density functional band structure calculations,<sup>9</sup> which suggest that the interface has the intermixed structure ···SiSiGaAsSiAs. Quite separate from nonideal heterovalent growth processes at the vacuum growth front is the aspect of interdiffusion within an already buried interface. At temperatures of 650 °C, Ge diffuses fractions of microns into GaAs,<sup>10</sup> with concentrations of  $10^{17}$ – $10^{18}$  cm<sup>-3</sup>. Since Ge acts as a *p*-type dopant in GaAs, this interdiffusion has the potential to substantially alter the heterojunction electronic properties.1

The above examples of chemically nonabrupt interfaces are all instances in which the deviation from ideality was

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unintentional. Intentional interlayer growth is sometimes performed, however, and it is thus important to determine the effects of such interlayers on the heterojunction band offsets. One reason for interlayer growth is to supply a buffer layer for accommodating strain due to lattice mismatch. Another reason is to create a barrier to interdiffusion. For example, Ga interlayers at a GeSi/Si(001) interface have been used to reduce Ge diffusion into the Si substrate.' A third reason for interlayer growth is for bond passivation. For example, the nonoctet bonds at the ideal ZnSe/Si(001) heterovalent interface can all be completely compensated by growth of a single As interlayer, to form a ···SiSiAsZnSe··· structure.<sup>11</sup> Finally, interlayers can be grown intentionally to alter the band offset across a junction: 1-2 ML of Si grown at the (001) GaAs/AlAs interface have been shown to alter the offset by up to 0.5 eV.<sup>12</sup> (This will be discussed in more detail in Sec. III.)

In summary, nonabrupt interfaces can be realized experimentally as a result of either interdiffusion (either postgrowth or during growth) or intentional interlayer growth. Furthermore, quaternary AB/CD systems allow two possible ideal (chemically abrupt) interfaces (either A-D or B-C). In the following, we explore the effects of such interfacial geometry variations on the band offsets across III-V/III-V (001) interfaces through the use of firstprinciple "computer experiments." In Sec. II, the specific methodology that is employed in these calculations is detailed. In Sec. III prior theoretical work on this problem is reviewed. Our main results and conclusions are presented in Secs. IV and V, respectively.

## **II. METHODOLOGY**

In the present section, we summarize the main aspects of our calculational procedure. The valence band offset across a heterojunction can be written

$$\Delta E_{v} = [E_{v} - \langle V \rangle]_{B} - [E_{v} - \langle V \rangle]_{A} + [\langle V \rangle_{B} - \langle V \rangle_{A}]_{IF}.$$
(1)

The first term on the right-hand side is the energy of the valence-band edge in pure material B with respect to the average potential  $\langle V \rangle_B$  in that material. The second term is the similar quantity in material A. Both of these band structure terms are properties of the bulk materials. These two terms have nothing to do with the A/B heterointerface, except for the fact that the strain configurations of pure materials A and B must be identical to the configurations of A and B on either side of the A/B interface. The third term in Eq. (1) is the interfacial dipole: the difference in the average potential on either side (but far from) the A/B interface. In the case of doped materials leading to space charge effects, the interface dipole must be evaluated on a length scale across which negligible band bending occurs. We denote the interface dipole as  $\Delta V_{\rm IF}$  below. Because it depends only on the charge density of the heterojunction, the interface dipole is a ground state property, and not a band structure (i.e., quasiparticle) property like the first two terms.

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-8.85 Ga Ga Ga Ga Ał AI AL AL (001) Direction -FIG. 1. Results of the present calculation of the valence band offset across a (001) GaAs/AlAs interface. The first two terms in Eq. (1) of the text are labelled  $\widetilde{E}_{v} = E_{v} - \langle V \rangle$  here. They result from two separate calculations of GaAs and AlAs zinc-blende compounds. The third interfacial dipole term in Eq. (1) is calculated to be 120 meV here. (Noncoulombic contributions due to the pseudopotential cores and the exchangecorrelation potential are included in this term.) This interfacial dipole was extracted from the calculated charge density of a (GaAs)<sub>4</sub>(AlAs)<sub>4</sub> (001) superlattice. A valence band offset (of the spin-orbit split states) of 490 meV is calculated. The conduction band offset of 220 meV is obtained from a rigid shift of the calculated conduction bands, in order that the experimental band gaps be obtained.

We use local<sup>13</sup> density functional theory<sup>14</sup> with *ab initio* nonlocal pseudopotentials<sup>15</sup> to calculate band offsets. Interpretation of the single particle eigenvalues in this theory as physical band energies, however, can lead to significant errors: band gaps are usually underestimated by about 50%, and even the quantities in the first two terms of Eq, (1) can contain small errors.<sup>16</sup> Using an approximate quasiparticle self-energy analysis, these latter errors have been shown to average about 120 meV for eight heterojunctions studied.<sup>17</sup> Figure 1 illustrates our calculation of a band offset. There we show the three terms in Eq. (1) for the case of GaAs/AlAs (001). The calculation results in a band offset of the spin-orbit split valence edge states of 490 meV, in good agreement with experiment<sup>18</sup> in spite of the fact that the quasiparticle corrections to the first two terms in Eq. (1) have been neglected.

The value of  $\Delta V_{IF} = 120$  meV shown if Fig. 1 is calculated (following the scheme of Baroni *et al.*<sup>19</sup>) as follows. A macroscopic average  $V_{macro}(z)$  of the potential V(x,y,z)

GaAs

2

AlAs

throughout the heterojunction is obtained from the relations

$$V_{\rm macro}(z) = \frac{1}{2l} \int_{-l}^{l} dz' \ \overline{V}(z+z'), \tag{2}$$

$$\overline{V}(z) = \frac{1}{A_{xy}} \int_{A_{xy}} dx \, dy \, V(x,y,z). \tag{3}$$

V(z) is a planar-averaged potential, i.e., it is the full potential V(x,y,z) averaged (over a two-dimensional unit cell  $A_{xy}$ ) in a plane parallel to the interface. Far from the interface, this planar-averaged potential V(z) is periodic over a 2 ML distance 21. This is a reflection of the fact that the charge density far from the interface is identical to that of the pure binary compound (GaAs or AlAs in the example of Fig. 1), and therefore that the potential in this region must be identical to the potential of the pure binary compound to within a constant. The macroscopic-averaged potential as defined in Eq. (2) is thus constant far from the interface, and the difference in the constant values on either side of the interface is simply the interfacial dipole  $\Delta V_{\rm IF}$ . In the case of a coherent strained-layer interface between two lattice-mismatched materials, the epitaxial constraint implies the constancy of the in-plane repeat area  $A_{xy}$  across the junction, but the existence of two different tetragonal deformations means that the macroscopic average in Eq. (2) must now be done with two different interplanar spacings,

$$V_{\text{macro}}(z) = \frac{1}{4l_1 l_2} \int_{-l_1}^{l_1} dz' \int_{-l_2}^{l_2} dz'' \ \overline{V}(z+z'+z'').$$
(4)

As in the lattice-matched case, the interfacial dipole  $\Delta V_{\rm IF}$  is simply the change in  $V_{\rm macro}(z)$  as the interface is crossed.

The main purpose of this article is to assess the manner in which the band offset across an interface varies with any variations in the atomic geometry of the interface. Because the only contribution to the band offset due to the interface itself is the interfacial dipole term  $\Delta V_{\rm IF}$ , the change in the band offset with some change in interfacial atomic geometry is completely and exactly simply the change in the interfacial dipole,

$$\Delta(\Delta E_v) = \Delta(\Delta V_{\rm IF}). \tag{5}$$

Since the main source of error in calculated band offsets comes from the quasiparticle error in the first two terms of Eq. (1), and since these terms cancel in calculating the change in the offset with a change in interfacial geometry, the offset changes can be calculated with an order of magnitude greater accuracy than the actual offsets themselves. Another source of error in calculated band offsets is non-completeness of the basis set and nonconvergence of Brillouin zone sums. These sources of error also substantially cancel in our present calculations of  $\Delta(\Delta V_{\rm IF})$ . Therefore, although local density functional calculated band offsets changes can be calculated with 10–20 meV, band offsets changes can be calculated with 10–20 meV accuracy.

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In all calculations reported here, (001) superlattice geometries have been used to represent the heterojunctions of interest. The repeat periods are sufficiently long (8-12 ML of each material, or 16-24 atoms per unit cell, were used) that the two interfaces per unit cell interact negligibly. The wave functions are expanded in plane waves with kinetic energies up to 9 Ry. (In some cases a 12-15 Ry energy cutoff was used to verify convergence.<sup>20</sup>) For the (001) heterojunctions considered here, there are two cell external degrees of freedom: the in-plane lattice constant  $a_{xy}$  and the overall lattice constant in the z direction  $a_{z}$ . The first of these  $(a_{xy})$  is determined by the epitaxial constraint of a coherent (or pseudomorphic) interface. For example, for the strained-layer case of InP on GaAs(001),  $a_{xy}$  is fixed to be the zinc-blende lattice constant  $a_{zb}$  of GaAs. (Calculated minimum-energy lattice constant, rather than experimental lattice constants, are used throughout this work. These are in general 0.5%-1.0% smaller than the experimental values.) In principle, the other cell external degree of freedom  $a_z$ , could be scanned and determined by an energy minimization procedure. When this was done with some short period superlattices [e.g., (GaAs)<sub>2</sub>(GaP)<sub>2</sub>], the result showed that the predictions of elasticity theory were verified to very high accuracy. Therefore, in dealing with the longer period superlattices used here to study interfacial geometry effects, elasticity theory layer spacings were used to determine an initial estimate of the cell-external  $a_{z}$ value. Consider, for example, the case of InP on GaAs(001) with an InAs interface. Because of the quaternary nature of this heterojunction, there are three different types of interplanar bonds: In-P, Ga-As, and (at the interface) In-As. Three different tetragonal distortions  $c/a_{xy}$ are thus calculated from elasticity theory, according to

$$\frac{c}{a_{xy}} = \frac{a_{zb}}{a_{xy}} + \frac{2c_{12}}{c_{11}} \left( \frac{a_{zb}}{a_{xy}} - 1 \right).$$
(6)

This leads to the following three (001) layer spacing  $\eta = c/(4a_{xy})$ :  $\eta$ (GaAs) = 0.25,  $\eta$ (InP) = 0.2706, and  $\eta(\text{InAs}) = 0.2876$ . The overall  $a_z$  value for a 24 layer unit cell composed of 12 GaAs monolayers, 10 InP monolayers, and 2 InAs (interfacial) monolayers is then  $a_z/a_{xy} = 12\eta$ (GaAs) +  $10\eta$ (InP) +  $2\eta$ (InAs). A similar procedure is used for the case of the GaP interface. Following this initial elasticity estimate of the atomic coordinates, the positions of the atoms within the unit cell are relaxed completely by moving the atoms until the calculated Hellmann-Feynman forces<sup>21</sup> on them vanishes. In general, the final equilibrium (zero-force) layer spacings differ slightly from the initial elasticity estimates. On occasion, this requires that the overall unit cell a, value be adjusted slightly from the initial elasticity estimate in order that layer spacings far from the interface are identical in the two heterojunctions being compared (e.g., InP/GaAs with a InAs versus GaP interface).

In summary, the effect of a change in interfacial structure on the band offset can be calculated quite accurately within density functional theory simply by calculating the change in the interfacial dipole. The importance of using, in all cases, equilibrium (i.e., zero-force) atomic geometries will be discussed further in Sec. IV.

#### **III. REVIEW OF PAST WORK**

There has, in the past, been several studies of the dependency of band offsets on interfacial structure. The interface-localized structural changes considered in these prior studies, and in the present study, can all be described as interface-localized composition changes. By this we mean the change from some (frequently ideal) interface geometry such as

to some other (generally nonideal) geometry, such as

$$\cdot -A - A - A - A - A - X - Y - B - B - B - B - B - B - \cdots \qquad (8)$$

We refer to the changes  $A \rightarrow X$  and  $B \rightarrow Y$  above as composition changes because they represent changes in the *identities* of the atoms located in those planes. In the case where the atomic planes labeled X and Y in Eq. (8) consist of alloyed mixtures of A and B atoms, we describe the nonideal geometry [Eq. (8)] as "chemically nonabrupt" or "intermixed." In the case where these X and Y planes consist of atoms not included in any of the A or B planes, we describe the geometry [Eq. (8)] as that resulting from the growth of a (foreign) interlayer. Yet another possibility exists in the case of noncommon-atom AB/CD (001) interfaces. In this case, one ideal (chemically abrupt) interface is

$$\cdots - A - B - A - B - A - B - C - D - C - D - C - D - \cdots , \qquad (9)$$

while another is

$$\cdots - A - B - A - B - A - B - A - D - C - D - C - D - \cdots$$
 (10)

The  $C \rightarrow A$  composition change above {that changes geometry [Eq. (9)] into geometry [Eq. (10)]} changes one chemically abrupt interface to another: from the B-C interface in Eq. (9) to the A-D interface in Eq. (10). In order to better understand the manner in which these composition changes affect interface dipoles, it is frequently convenient to consider the changes as resulting from<sup>8</sup> "theoretical alchemy," whereby the composition change occurs as a result of the transmutation of atomic identity, and this transmutation is treated as a perturbation to the original Hamiltonian. We shall employ this concept often in analyzing the results of the past and present calculations.

In order to understand the major themes that emerge from past studies, it is convenient to separate the isovalent composition changes (e.g.,  $As \rightarrow P$ , where valency is conserved) from heterovalent ones (e.g.,  $As \rightarrow Si$ , which does not conserve valency). A major result of the past work is the following: heterovalent composition changes that lead to an overall valency change in a direction not parallel to the interface can lead to large (on the order of 1 eV) band offset changes. This result was originally obtained by Harrison *et al.*<sup>8</sup> through use of simple electron-counting arguments. We exemplify it with two specific results: First, consider an (001) Si/GaAs interface. Because of the existence of nonoctet bonds, the ideal interfaces,

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or

$$\cdots$$
-Si-Si-Si-Si-Si-Si-As-Ga-As-Ga-As-Ga- $\cdots$ , (12)

···-Si-Si-Si-Si-Si-Ga-As-Ga-As-Ga-As-

are extremely unstable. (They are, in fact, metallic<sup>22,23</sup> due to uncompensated interface bonds.) They therefore reconstruct into interfaces that have all nonoctet bonds self-compensated,<sup>22,23</sup> such as

$$\cdots - Si - Si - Si - Si - Si - Si - Ga_{0.5}Si_{0.5} - As - Ga - As - Ga - As - \cdots$$
(13)

or

We ask whether the band offset across the semiconducting interfaces [Eqs. (13) and (14)] is altered as a result of the different interfacial geometry in the two cases. Notice that the interface of Eq. (13) can be transformed into the interface of Eq. (14) via a composition change in two atomic planes, which transform the Si-Ga<sub>0.5</sub>Si<sub>0.5</sub> interface with average valences 4-3.5, to the  $As_{0.5}Si_{0.5}$ -Ga interface with average valences 4.5-3. Within the theoretical alchemy picture mentioned above (and within a pseudopotential treatment of frozen cores) the composition change from Eqs. (13) to (14), thus results in 0.5 protons being moved from right to left between interface planes. This valence change orthogonal to the interface is screened only incompletely by the ensuing ionic and electronic relaxation. We thus expect a large difference in the band offsets between interfaces [Eqs. (13) and (14)]. Indeed, density functional calculations have verified this simple picture. The offset of Eq. (13) has been calculated<sup>22</sup> to be 0.3 eV (Si higher), while that of Eq. (14) is found to be 0.5 eV (with GaAs higher), resulting in an offset change of 0.8 eV between the two interfaces. This result is in good agreement with the simple dielectric-screening-of-proton-transfer model.<sup>19</sup> Analogous calculations have been done on Ge/GaAs and Si/GaP<sup>22,23</sup> showing similar results. A second example of a heterovalent composition change inducing a band offset change is the theoretical prediction of Baroni et al.<sup>19,24</sup> and Munoz et al.<sup>25</sup> who suggested that growth of a column IV bilayer within an (001) interface between two III-V materials like GaAs/AlAs should lead to a large change in offset across the GaAs/AlAs junction, and that controlling the amount of column IV material grown in the interlayer should allow one to tune the band offset controllably. These predictions were verified to a large extent by the experimental work of Sorba et al.<sup>12</sup> who demonstrated a controllable variation of 0.5 eV of the GaAs/AlAs offset with Si interlayer growth.

Another study of the effect of interlayer growth on band offsets was done by Christensen and Brey.<sup>26</sup> They calculated the effect on the band offset due to interlayers within the nonpolar (110) interfaces of GaAs/AlAs, AlAs/Ge, AlP/Si, and CdTe/InSb (all of which are nearly latticematched). Within their calculational uncertainty, they found only CuBr to have a noticeable effect on the band

(11)

offset (altering the AlAs/Ge offset by 280 meV, for example). All other interlayers made no noticeable effects, including heterovalent interlayers like Ge at the GaAs/AlAs interface (because in this case the proton transfer occurring in the theoretical alchemy described above takes place *parallel* to the interface).

Having considered the large effect on band offsets resulting from certain heterovalent interfacial composition changes, we next examine previous studies of the effects of isovalent composition changes. One important result has emerged from the linear response theory of Baroni et al.,<sup>19</sup> who consider the evolution of a heterojunction's charge density from that of a parent virtual crystal approximation (VCA) binary compound: GaAs/AlAs, for example, can be obtained by changing half the virtual  $\langle AlGa \rangle$  cations in a zinc-blende (AlGa)As compound into Al, and the other half into Ga. They have demonstrated the following elegant result for lattice-matched heterojunctions with a common atom: if the total change in charge density upon this VCA parent  $\rightarrow$  heterojunction transformation is identical to that of the sum of single-atom-at-a-time changes (i.e., if the transformation process is linear), then the final band offset is independent of any isovalent interfacial geometry. This follows simply by symmetry: a single-atom transformation (a lone  $\langle A|Ga \rangle \rightarrow Al$  change in the otherwise ideal zinc-blende (AlGa)As material, for example) cannot induce an extra dipole by symmetry; by the linearity assumption, single atom composition variations at the heterointerface thus also cannot induce any change in dipole. The assumption of linearity has been tested and verified to very high accuracy for the case of GaAs/AlAs. The reason the theorem has been demonstrated to hold in general only for lattice-matched systems is that even a single-atom transformation that includes a shift of nuclear coordinates (which would occur in a strained-layer system) can cause an additional dipole (except for the case of nonpolar materials like Si/Ge, where the Born effective charges vanish). Thus far, no linear response theory has been developed that demonstrates the independence of offsets on interfacial geometry in lattice-mismatched cases. The reason the common-atom requirement is also added is that, in general, a lattice-matched quaternary AB/CD system will have interfacial layer spacings (B-C or A-D) that differ from the identical A-B and C-D spacings, again causing some shifts of nuclear coordinates in the VCA parent  $\rightarrow$ heterojunction transformation. Baroni et al.<sup>19,27</sup> have, however, demonstrated that if the lattice-matched quaternary  $Ga_{0.47}In_{0.53}As/InP$  is treated as purely cubic, i.e., if the difference between the interfacial interlayer spacings and the spacings elsewhere are neglected, then the heterojunction charge density is indeed linearly related to its parent VCA compound, meaning the heterojunction offset is independent of any isovalent interfacial composition changes. Similarly, they have shown<sup>28</sup> that when a strained layer Si/Ge heterojunction is also treated as cubic (another gedanken experiment) linear response theory again applies. Since the Born effective charges nearly vanish throughout this cubic heterojunction, changing its layer spacings to those of a real Si/Ge strained-layer system will

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not further add to the offset. They thus have given some understanding to the previously demonstrated result of Hybertson<sup>29</sup> that the Si/Ge offset is independent of any interfacial intermixing. Hybertson<sup>30</sup> also has done a careful study of the lattice-matched Ga<sub>0.47</sub>In<sub>0.53</sub>As/InP band offset outside the context of linear response theory. Including the correct interfacial layer spacings (which are different from those away from the interface) he has shown that the offset is independent of which of the two chemically abrupt interfaces occurs (i.e., InAs or Ga<sub>0.47</sub>In<sub>0.53</sub>P). He has also shown that As–P intermixing in the anion planes near the interface does not alter the band offset.

In summary, several previous theoretical studies have demonstrated that heterovalent interfacial composition changes can lead to large offset variations. With regard to isovalent changes in interfacial geometry, linear response theory suggests that lattice-matched common-atom systems exhibit offsets independent of such changes. Such changes have also been shown to cause no offset variation in the lattice-matched quaternary  $Ga_{0.47}In_{0.53}As/InP$ , and also in the lattice-mismatched but nonpolar Si/Ge system. Our purpose here is thus to look for variations in offsets due to isovalent changes in interfacial geometry in latticemismatched III–V systems, and in quaternary systems other than the lone case considered above.

# IV. RESULTS: BAND OFFSET DEPENDENCY ON INTERFACIAL STRUCTURE

In this section we present the results of calculations of the dependence of band offsets on interfacial atomic structure. We first discuss, in Sec. IV A, the importance of obtaining the correct equilibrium (i.e., zero-force) atomic geometry near the interface. We then present our main results: isovalent interfacial composition changes cause no change in band offsets in common-atom systems (even those with large lattice-mismatch), whereas such geometry changes can lead to small but nonnegligible offset changes in some quaternary systems. A theoretical framework for understanding these results, based on the nearest-neighbor symmetry of the site undergoing a composition change, is present in Sec. IV B. Specific results that demonstrate this principle for common-atom and noncommon-atom systems are presented in Secs. IV C and IV D, respectively.

## A. Interfacial atomic relaxations and band offsets

The positions of nuclei near a coherent interface between two materials are not simply those positions obtained by layering truncated bulk (possibly strained) assemblies of the two constituents on top of each other. Rather, nuclei near the interface are shifted by the charge redistribution caused by the interface itself. In the case of coherent lattice-mismatched interfaces (i.e., strained-layer interfaces) the major cause of these interface-localized relaxations is that of strain relief: the decreased symmetry of atoms near the interface allows such atoms to shift position very slightly to bring their bond lengths and bond angles closer to their unstrained values. These interface-localized strain relieving relaxations were studied by us previously for a large number of systems.<sup>31</sup> There we found that these



FIG. 2. (a) Calculated variations in interlayer spacings throughout the (001) AlP/InP interface.  $\eta_0$  is the layer spacing (in units of  $a_{xy}$ ) far from the interface:  $\eta_0(\text{InP}) = 0.2690$  and  $\eta_0(\text{AlP}) = 0.2323$ . (b) Change in the planar-averaged potential  $\overline{V}(z)$  between the equilibrium (zero-force) geometry shown in (a) and the constant layer spacing geometry. Note that the interface-localized relaxations induce a 58 meV dipole that raises the AlP part of the junction.

relaxations are very large and can extend far from the interface in higher index growth directions such as (110) and (201), but are considerably smaller and much more interface-localized in the (001) and (111) directions. The purpose of this section is to demonstrate the significance of these small relaxations within (001) interfaces on the band offset.

To this end we consider an (001) interface between AIP and InP. The calculated zinc-blende lattice constants of these materials are a(AlP) = 5.439 Å and a(InP) = 5.831Å, resulting in a large 7% lattice mismatch. We consider an epitaxially constrained system where  $a_{xy} = a_{avg} = 5.635$ Å. In such a system, elasticity theory predicts that the tetragonal deformations result in the following layer spacings:  $\eta_{\text{elast}}(\text{AlP}) = 0.2325$  and  $\eta_{\text{elast}}(\text{InP}) = 0.2685$ . We thus begin our calculation of a 16 layer (001) (AlP<sub>4</sub>(InP)<sub>4</sub> superlattice by layering 8 AIP planes separated by  $0.2325a_{xy}$  on top of 8 InP planes separated by  $0.2685a_{xy}$ . Relaxing the Hellman-Feynman forces on this geometry results in a zero-force equilibrium geometry where the central 6 of the 8 AlP layers are separated by  $\eta_0(AlP) = 0.2323$ , and the central 6 of 8 InP layers are separated by  $\eta_0(\ln P) = 0.2690$ , demonstrating the accuracy of the initial elasticity estimate. However, the AlP and InP layers immediately next to the interface have layer spacings about 1.5% less than and greater than, respectively, their values far from the interface. These are the small interface-localized relaxations referred to above. They are plotted throughout the 16 layer supercell in Fig. 2(a). There it can be seen how rapidly the layer spacings approach their far-from-the-interface values: after the

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1.5% variation immediately next to the interface, subsequent layer spacings vary by less than 0.1%. The major relaxation is simply a shift of the interface P atoms (those in the configuration In-P-A1) away from In and towards Al. The small relaxations seen in Fig. 2(a) are actually brought about by the quest for the atoms near the interface for *strain relief*: the relaxations result in the In-P and Al-P bond lengths at the interface to be nearer their unstrained zinc-blende values.

In order to determine the effects of these small interfacelocalized relaxations on the band offset, we perform a third calculation, where 8 AlP layers separated by  $\eta_0(AlP)$  are stacked on top of 8 InP layers separated by  $\eta_0(InP)$ . The atomic coordinates of this geometry differ from those of the equilibrium zero-force geometry only with respect to atomic planes at the interface. In order to find the change in band offset induced by the interface-localized relaxations, we need only subtract the potential of the unrelaxed geometry from that of the relaxed geometry. This is done in Fig. 2(b), where it is seen that the interface-localized relaxations create a dipole that raises the AIP half of the junction by 58 meV. In order to demonstrate that the major cause of these interface-localized relaxations is interfacial strain due to lattice mismatch, a similar calculation as above was also performed for the nearly lattice-matched cases of AlAs/GaAs and Ga<sub>0.47</sub>In<sub>0.53</sub>As/InP. In both cases the relaxations were much smaller than in the AlP/InP case, and their effect on the band offset was found to be less than 10 meV. Our conclusion, therefore, is that obtaining the correct zero-force equilibrium geometry in strainedlayer heterojunctions is crucial for calculating accurate offsets and accurate changes in offsets with changes in interfacial composition.

# B. Symmetry and composition-change-induced dipoles

In this section we describe a framework for understanding the results of our computer experiments. In these calculations, we make isovalent composition changes localized near a III-V/III-V (001) interface, and determine the effect of these geometry changes on the band offset. In our present work, these geometry changes have all been made without introducing any foreign atoms into the system. For common-atom AC/BC systems, we consider only the effect of A-B intermixing in the noncommon-atom planes near the interface, as would result from interdiffusion processes. For noncommon-atom AB/CD systems, apart from such intermixing, we also consider composition changes that transform one chemically abrupt interface into another. There is an important difference between the common-atom and noncommon-atom composition changes: all such changes occurring in the common-atom system occur at lattice sites with nearest-neighbor mirror symmetry about a plane through the site and parallel to the interface, whereas this need not be the case in quaternary AB/CD systems. For example, the change in AC/BC from the ideal

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$$\cdots - A - C - A - C - A - C - B - C - B - C - B - C - \cdots$$

$$(15)$$

interface to an intermixed

$$\cdots - A - C - A - C - A - C - A_x B_{1-x} - C - B - C - B - C - (16)$$

interface takes place on atomic sites B that, at the level of nearest neighbors, have mirror symmetry (having B-C bonds of nearly identical length both left and right). However, the composition change in AB/CD that transforms the chemically abrupt B-C interface

$$\cdots - A - B - A - B - A - B - C - D - C - D - C - D - \cdots$$

$$(17)$$

into the chemically abrupt A-D case

$$\cdots -A - B - A - B - A - D - C - D - C - D - C - D - \cdots$$
(18)

is that of changing A–B–C into A–D–C. This  $B \rightarrow D$  transformation occurs at a site without mirror symmetry at even the nearest-neighbor level.

The effect of this symmetry (or lack thereof) on the induced dipole following the composition change is as follows. Recall that a composition change of an isolated (001) plane within a zinc-blende binary compound such as changing

$$\cdots - A - B - A - B - A - B - A - B - A - B - A - B - \cdots$$
(19)

into

$$\cdot -A - B - A - B - A - B - X - B - A - B - A - B - \cdots$$
(20)

cannot induce any extra dipole by symmetry. The induced change in charge density has perfect left-right symmetry, and thus has no dipole moment. In the common-atom case of geometry [Eq. (15)] changing to geometry [Eq. (16)] this rigorous result fails only in that the mirror symmetry is violated at second-nearest-neighbor distances. It is expected then that the induced dipole is quite small in this case. In the noncommon-atom case of geometry [Eq. (17)] changing into geometry [Eq. (18)], this failure occurs at the first-nearest-neighbor distance. Thus, it is possible that the left-right asymmetry of the induced charge density variation is sufficient to create a non-negligible dipole. This is what is found in our calculations. We demonstrate this result with specific examples in Secs. IV C and IV D.

## C. Common-atom systems

In this section we demonstrate the null effect of interfacial composition changes resulting from intermixing on the band offsets across lattice-mismatched common-atom systems. Recall from Sec. III that the motivation for posing this question is the fact that from past work, the independence of offsets to isovalent interfacial compositional changes has been demonstrated in the lattice-matched cases of GaAs/AlAs and Ga<sub>0.47</sub>In<sub>0.53</sub>As/InP, and in the lattice-mismatched (but nonpolar) case of Si/Ge. In the case of Si/Ge, the strain effects do not cause any extra dipoles due to the nonpolar nature of the bonding. In this section we consider two test cases of common-atom systems: AlP/InP and GaAs/GaP, which have large lattice mismatches of 7% and 4%, respectively. These large lattice mismatch systems were chosen as extreme test cases. We examined several nonideal interface geometries. Our results can be simply stated: We find no change in the band offset with isovalent composition changes at either the AlP/InP or GaAs/GaP interfaces, in spite of the large atomic relaxations induced by the composition changes in these strained-layer systems.

Consider first the case of AlP/InP. The ideal atomically abrupt interface has the atomic arrangement

$$\cdots - Al - P - Al - P - Al - P - In - P - In - P - In - P - \cdots$$
 (21)

A general atomic configuration of a nonabrupt interface obtained by alloying (i.e., mixing) in the cation planes immediately adjacent to the interface P plane can be represented as

$$\cdots -Al - P - Al - P - (Al_x In_{1-x}) - P - (Al_y In_{1-y}) - P - In - P - In - P - \cdots$$
(22)

The ideal interface in Eq. (21) is (x = 1, y = 0). We performed calculations of the change in interface dipole induced by alloying for several nonideal cases: (0.5,0.5), (0.5,0), and (0,1). In the (0.5,0) case, the alloyed plane  $Al_{0.5}In_{0.5}$  was treated within a VCA, whereby a single virtual cation was used whose pseudopotential is simply the average of the Al and In pseudopotentials. In the case of the (0.5,0.5) test, two separate calculations were performed. In one the VCA approximation was used again. In the second, a  $\sqrt{2} \times \sqrt{2}$  reconstruction of the supercell was used, and an ordered arrangement of Al and In decorated the cation planes immediately adjacent to the interface. In the  $\sqrt{2} \times \sqrt{2}$  case, the supercell consisted of only 6 ML of each material, and only one of the two interfaces in the supercell was mixed. In all other cases the supercell consisted of 12 ML of each material, and both interfaces were mixed. In all four test cases of nonabrupt intermixed interfaces, no extra interface dipole  $\Delta V_{\rm IF}$  was found compared to the ideal chemically abrupt interface. The results of the calculation for the (0,1) case are shown in Fig. 3. There the change in the interface dipole is decomposed into two terms: that due to the coulomb potential of the bare ions, and that due to the coulomb potential of the electrons. It is seen that although both the ionic and electronic potential changes each have large 35 eV dipoles associated with them, these dipoles exactly cancel [see Fig. 3(c)], and the overall potential change vanishes upon intermixing. The reason the ionic potential change contains a dipole is simple: trading a large In atom on the right for a small Al atom on the left results in relaxations of the nuclear coordinates whereby the five atomic planes centered at the interface all shift to the right. This shift of nuclei creates the bare ion dipole shown in Fig. 3(b) (solid line). The electronic charge rearrangement that screens this change in bare ion potential is shown in Fig. 3(a). The dipole created by this electron arrangement is shown in Fig. 3(b) (dashed line). Its exactly opposite character to the ionic dipole is apparent.

It is interesting to compare the difference between this lattice-mismatched case and intermixing within a latticematched interface, such as that following cation intermix-

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FIG. 3. (a) Change in the valence electron charge density following Al–In intermixing at the (001) AlP/InP interface. (b) Potential changes following the above intermixing. The solid line is the change in the bare ion potential, while the dashed line is the change in the coulomb potential due to the electrons (i.e., the Hartree potential). (c) The sum of the solid and dashed lines in (b), demonstrating that the dipoles there exactly cancel. Actually, the value of the additional dipole extracted from (c) is  $\Delta(\Delta V_{\rm IF}) = 1.7$  meV, which is zero within our calculational uncertainty.



FIG. 4. (a) Change in the valence electron charge density following Al-Ga intermixing at the (001) AlAs/GaAs interface. Note that (in contrast to Fig. 3) only one interface is shown here. The cation planes labeled M denote 50:50 mixed Al-Ga planes (ordered in a  $\sqrt{2} \times \sqrt{2}$  pattern). In the unmixed geometry the left M is Al and the right M is Ga. Note that overall, charge is transferred from right to left following the intermixing (i.e., the charge follows the Ga overall). (b) Potential change produced by the electronic charge redistribution in (a). Note that no extra dipole is induced.

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ing at the lattice-matched GaAs/AlAs interface. We have calculated the effect of such intermixing on the band offset, and find, as expected from previous work,<sup>19</sup> no change, just as for AlP/InP above. However, as is shown in Fig. 4, the different character to the lattice-mismatched case is apparent. Because intermixing Al and Ga leads to no shift in nuclear coordinates (in the present approximation of neglecting the small lattice mismatch between GaAs and AlAs), the bare ion contribution to the dipole change exactly vanishes. This means that, in spite of an overall electronic charge transfer from Al to Ga following the intermixing (Ga is more electronegative that Al), this electronic charge rearrangement must also produce zero dipole. Figure 4(a) shows the electronic density change induced by the intermixing, and Fig. 4(b) shows that this charge rearrangement indeed produces no extra dipole. In the lattice-matched case the ionic and electronic dipole changes are thus individually zero. In the latticemismatched case, they are both nonzero, but sum to zero because they are equal and opposite.

With regard to GaAs/GaP, two mixed interface tests were performed: that of the  $\sqrt{2} \times \sqrt{2}(0.5,0.5)$  and that of the VCA (0.5,0) geometries defined above. As in the case of AlP/InP, no extra interfacial dipole  $\Delta V_{\rm IF}$  was created by the anion intermixing. The band offset of the ideal interface is the same as the band offset of the nonabrupt interfaces, to within our calculational uncertainty of 10 meV. Both of these AlP/InP and GaAs/GaP cases demonstrate that composition changes occurring at sites of nearest-neighbor symmetry do not cause a noticeable change in the interfacial dipole. In Sec. IV D, we demonstrate how noncommon-atom systems allow for the opposite result.

## D. Noncommon-atom quaternary systems

In this section we present the results of calculations that show that composition changes within quaternary III-V (001) interfaces can result in some small change of the band offset. In particular, we test three systems: GaAs/ AlSb, GaAs/InP, and InAs/GaSb, with calculated lattice mismatches of 7%, 4%, and 0.6%, respectively. In the case of GaAs/InP, the calculation is performed with the epitaxial constraint of a GaAs substrate  $(a_{xy} = a_{GaAs})$ . In the other two cases the calculations are done with the epitaxial constraint  $a_{xy} = a_{avg}$ . The two different chemically abrupt interfaces are found to have offsets that differ by 77 meV in the case of GaAs/AlSb, by 44 meV in the case of InAs/ GaSb, and by only 4 meV in the case of GaAs/InP. Furthermore, intermixing within the GaAs/AlSb interface is found to cause offset changes of up to 83 meV. We describe these results below, and show how the model of nearestneighbor asymmetry adds to their understanding.

We first demonstrate the change in interfacial dipole between the abrupt AlAs and GaSb interfaces of GaAs/ AlSb. In the case of the AlAs interface,  $\Delta V_{IF}$  was obtained from a calculation using a supercell of 10 ML of GaAs, 8 ML of AlSb, and 2 (interfacial) ML of AlAs. Transmuting an interfacial Al to a Ga (and adjusting the nearby layer



FIG. 5. Macroscopic averaged potential  $V_{\rm macro}(z)$  for the two different interfaces of GaAs/AlSb (001). Squares label cation positions and hatches label anion positions along the (001) direction. The AlAs (GaSb) interface calculation was performed in a supercell consisting of 10 (8) ML of GaAs, 8 (10) ML of AlSb, and two interfacial monolayers of AlAs (GaSb). The interfacial dipole  $\Delta V_{\rm IF}$  is 931 meV (854 meV) in the case of the AlAs (GaSb) interface.

spacings slightly to maintain an equilibrium geometry) changes the AlAs interface

$$\cdots$$
-Ga-As-Ga-As-Ga-As-Al-Sb-Al-Sb-Al-Sb-Al-Sb-(23)

into the GaSb interface

$$\cdots$$
-Ga-As-Ga-As-Ga-As-Ga-Sb-Al-Sb-Al-Sb-(24)

This isovalent composition change is performed in an environment lacking nearest-neighbor symmetry, and results in an induced charge density change that creates a 77 meV large dipole (that lowers AlSb with respect to GaAs). This extra dipole is shown in Fig. 5, where  $V_{\rm macro}(z)$  is plotted for heterojunctions with both interfaces. A similar result is found for the nearly lattice-matched case of InAs/GaSb: changing from the abrupt InSb interface

$$\cdots$$
-As-In-As-In-As-In-Sb-Ga-Sb-Ga-Sb-Ga-(25)

to the abrupt GaAs interface

by an In  $\rightarrow$  Ga change (with the accompanying changes in lattice spacings) creates an addition to the interfacial dipole  $\Delta V_{IF}$  that raises the InAs 44 meV. In the third test system studied (GaAs/InP), however, only a 4 meV offset variation was found between the heterojunction with a InAs and GaP interface. (This is within the error bars of the calculation.) Combining these results with the previous result on Ga<sub>0.47</sub>In<sub>0.53</sub>As/InP,<sup>30,32</sup> we have demonstrated offset dependency on interfacial identity in two systems (lattice-matched InAs/GaSb and lattice-matched GaAs/ AlSb), and offset independency on interfacial identity in two other systems (lattice-matched Ga<sub>0.47</sub>In<sub>0.53</sub>As/InP and lattice-mismatched GaAs/InP). These results are summarized in Table I under the  $\Delta(\Delta V_{IF})_{equil}$  column. Thus, it is possible in some cases that the combination of chemical and strain perturbations that transform one interface into

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TABLE I. Calculated change in the interface dipole (and thus in the band offset) for the two different chemically abrupt interfaces of four quaternary (001) heterojunctions. For the lattice mismatched systems, the epitaxial constraint is denoted by the value of  $a_{xy}$ , and  $\Delta a/a$  is the calculated fractional lattice mismatch. In order to isolate the contribution of strain to the variation of interfacial dipole with interface geometry, the  $\Delta(\Delta V_{\rm H})$  values are given both for the equilibrium geometry, and also for a (gedanken experiment) geometry where the atoms are kept on a cubic zinc-blende mesh. The sign convention for the reported  $\Delta(\Delta V_{\rm HF})$  values is such that a positive value indicates a raising of the potential in AB when the AB/CD interface is changed from B-C to A-D.

Heterojunction	a <sub>xy</sub>	Δa/a	$\Delta (\Delta V_{1F})_{equil}$ (meV)	$\Delta (\Delta V_{\rm lf})_{\rm cubic}$ (meV)
GaAs/AlSb	a <sub>ave</sub>	7%	77	36
InAs/GaSb	aave	0.6%	- 44	- 36
GaAs/InP	a <sub>GaAs</sub>	4%	4	- 28
Ga <sub>0.47</sub> In <sub>0.53</sub> As/InP		≈0	≈0	≈0

another add up in such a manner that no offset variation is found. The present calculations show only the possibility (not the necessity) of having offsets dependent on interfacial geometry in quaternary (001) systems.

The contribution to the offset variation due to strain effects can be approximately isolated by performing gedanken experiment calculations where all the nuclei of the quaternary system sit on a cubic zinc-blende mesh. The results of these calculations are summarized in Table I under the  $\Delta(\Delta V_{\rm IF})_{\rm cubic}$  column. In the context of the linear response theory discussed above,<sup>19</sup> any variation in the interface dipole in the cubic geometry cases can be exactly construed as nonlinear effects. We thus see that these strain-free nonlinear effects vanish only in the case of Ga<sub>0.47</sub>In<sub>0.53</sub>As/InP, where the equilibrium geometry also showed no offset variation. It is interesting that in the other case (of GaAs/InP) where we found offset independence on interfacial geometry, the strain effect approximately cancels the nonlinear strain-free contribution. In the other two cases the strain effect adds to the nonlinear strain-free part. In the case of GaAs/AlSb, in fact, it more than doubles that contribution of 36 meV, resulting in a total offset variation of 77 meV.

We next consider the effect of intermixing within the GaAs/AlSb interface. In particular, we exchange As and Sb in the interface anion planes of the chemically abrupt AlAs interface shown in Eq. (23) above, resulting in the following nonabrupt interface.

$$\cdots$$
-Ga-As-Ga-As-Ga-Sb-Al-As-Al-Sb-Al-Sb- $\cdots$  . (27)

The nearest-neighbor symmetry model (detailed in Sec. IV B above) predicts that the intermixed interface [Eq. (27)] should exhibit a band offset identical to that of the chemically abrupt GaSb interface [Eq. (24)]. This follows because the geometries [Eqs. (27) and (24)] are simply related by a change from Al–Sb–Al in Eq. (24) to Al–As–Al in Eq. (27), a composition change that occurs at a site with nearest-neighbor symmetry and should thus not induce a significant offset change. Our calculations validate this prediction: the intermixed geometry [Eq. (27)] is

found to have an offset 6 meV different than the abrupt geometry [Eq. (24)]. Stated another way, changing from the abrupt geometry [Eq. (23)] (with an AlAs interface) to the intermixed geometry [Eq. (27)] creates an addition to the interfacial dipole that raises the GaAs part of the junction by 83 meV. This result demonstrates a connection between the variation in offsets between the two abrupt interfaces of a quaternary system, and the possible variation in offset resulting from intermixing. Also, if we consider the 50-50 intermixed interface

$$\cdots$$
-Ga-As-Ga-As-Ga-As<sub>0.5</sub>Sb<sub>0.5</sub>-Al-Sb-Al-Sb-(28)

we find an offset nearly midway between those of the geometries (23) and (27): in going from Eq. (23) to Eq. (28) the GaAs part of the junction is raised 48 meV. This suggests that the offset changes are approximately linear in the composition changes that bring them about.

## **V. CONCLUSIONS**

In this article we have considered the effect of isovalent composition changes at (001) interfaces of III-V materials. For the case of common-atom AC/BC systems, we have considered the effect of intermixing in the A-B planes near the interface. For both the AlP/InP and GaAs/GaP systems considered, such intermixing was found to have no effect on the band offsets. In the case of noncommon-atom AB/CD systems, we have shown how the two different chemically abrupt interfaces can have different band offsets, and how intermixing can lead to a similar change in offset. A simple model was suggested to comprehend these results for the (001) systems currently studied. According to this model, composition changes occurring at a site with nearest-neighbor symmetry do not lead to substantial offset changes (leading to changes less than 5 meV according to our calculations), while composition changes occurring at a site lacking nearest-neighbor symmetry can lead to significant offset changes. We have demonstrated that such composition changes lead to nonzero effects on the band offsets in the cases of GaAs/AlSb and InAs/GaSb heterojunctions. Within the context of linear response theory, these offset changes can be construed as nonlinear effects. In the case of  $Ga_{0.47}In_{0.53}As/InP$ , these nonlinear effects vanish. In the case of GaAs/InP, the strain contribution to the offset variation cancels the nonlinear strain-free contribution, resulting in an offset independent of interfacial geometry. When compared to the large ( $\approx 0.5 \text{ eV}$ ) offset changes resulting from heterovalent composition changes, the isovalent effects found in the present work are quite small, being 83 meV in the largest case. They should nonetheless be observable.

Note added in proof: After submission of this manuscript, Y. Foulon and C. Priester have published tightbinding calculations [Phys. Rev. B 45, 6259 (1992)] that find some results similar to those presented here. However, they find substantial band offset variation between the two chemically abrupt interfaces of Ga<sub>0.47</sub>In<sub>0.53</sub>As/InP and GaAs/InP (of 65 and 80 meV, respectively) whereas we find negligible band offset changes in these systems (see

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Table I and Refs. 30 and 32). See also the manuscript of G. Allan et al. in these conference proceedings.

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- <sup>32</sup>As a check on our present calculations we redid the calculations on Ga0.47In0.53As/InP, and find, in agreement with Ref. 30, the same offsets for the two different chemically abrupt interfaces. These new calculations were done with supercells with identical interfaces, so that any offset change would be easily identifiable.