Band Offsets in Lattice-Matched Heterojunctions: A Model and First-Principles Calculations for GaAs/AlAs

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A new model for band offsets in lattice-matched heterojunctions is presented along with a novel definition of the interface dipole which avoids any reference to an ideal interface. The model is derived only from the charge densities of the bulk constituents and naturally predicts the independence of the offsets on interface geometry. It is in excellent agreement with accurate first-principles pseudopotential calculations for $(GaAs)_3/(AlAs)_3$ grown in the (001), (110), and (111) directions and with available experimental data.

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In recent years much interest[1-8] has been devoted to band offsets at semiconductor heterojunctions. Because of the long-range nature of Coulomb interactions, the offsets depend not only on the properties of the two bulk materials, but also on the electronic distribution at the interface[2] which in principle depends on the interface geometry. For the most studied system, namely GaAs/AlAs, previous first-principles calculations indicate that (001), (110), and (111) interfaces have similar offsets.[2,3] Experiments indicate at most a weak dependence on orientation and growth sequence.[7] The present experimental accuracy, however, is not high: The most reliable data for the valence-band offset in GaAs/AlAs range from 0.40 to 0.55 eV.[8]

The average of the electrostatic potential in an infinite solid is an ill-defined constant.[9] The lineup of the average electrostatic potential across the interface between two semi-infinite solids is, on the contrary, well defined and the band offset is obtained by addition of it to the bulk band-edge difference resulting when the arbitrary average values of the electrostatic potentials in the two materials are aligned. Only the lineup due to the Hartree potential is explicitly considered here, because the ionic potentials give only a short-range contribution to the lineup which is implicitly accounted for in the bulk band-edge difference. We have performed state-of-the-art density-functional-theory (DFT) calculations for $(GaAs)_3/(AlAs)_3$ superlattices oriented in the (111), (110), and (001) directions. We use the local density approximation (LDA),[10] plane-wave (PW) basis sets up to a kinetic energy of 14 Ry (about 1550 PW's for our twelve-atom supercells), norm-conserving pseudopotentials,[11] and Ceperley-Adler[12] exchange-correlation data; **k**-space integrations have been performed with the special-point technique: We have used the (444) Monkhorst-Pack cubic mesh[13] appropriately folded for the three geometries. The actual number of special points is 2, 4, and 5 for the (001), (110), and (111) interfaces, respectively. Convergence studies with respect to the number of **k** points and the size of both the basis set and the supercell have been performed in order to guarantee an accuracy of ~0.01 eV.

The physical quantities $f(\mathbf{r})$ we are interested in [such as the electron density $n(\mathbf{r})$ or the electrostatic potential energy $V(\mathbf{r})$] are periodic in the planes perpendicular to the growth direction (z axis). As we are mainly interested in the z dependence of such quantities, it is convenient to define $\bar{f}(z)$ as the xy planar average of $f(\mathbf{r})$. The function $\bar{f}(z)$ is nonperiodic in the interface region, and goes asymptotically into two different periodic functions (having the same period for lattice-matched heterojunctions) far from the interface: A typical result for the self-consistent charge density $\bar{n}(z)$ and potential $\bar{V}(z)$ of $(GaAs)_3/(AlAs)_3$ (111) is shown in Fig. 1(a). The strong atomic oscillations are bulklike and hide interface effects, such as the barely visible potential shift across the interface. In order to get rid of bulk effects and to blow up interface features, it has been proposed[3,4] to define a function $\Delta\bar{f}(z)$ subtracting, on each side of the interface, the appropriate bulk function from $\bar{f}(z)$: This is illustrated in Fig. 1(b). The relevant features of this construction are as follows: (i) The interface region cor-

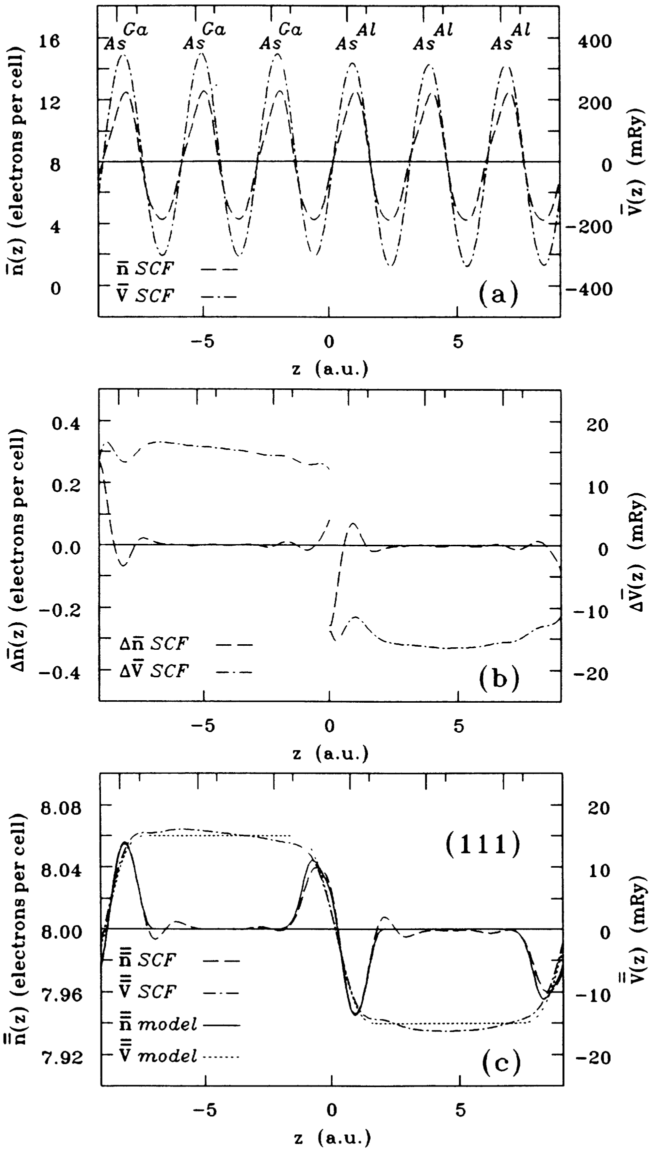

FIG. 1. (a) Planar average of the first-principles (SCF) electron density $\bar{n}(z)$ and electrostatic potential energy $\bar{V}(z)$ of $(\mathrm{GaAs})_3/(\mathrm{AlAs})_3$ oriented along (111). (b) Difference between the planar averages in (a) and the corresponding quantities in the bulk materials [$\Delta\bar{n}(z)$, $\Delta\bar{V}(z)$]. The arbitrary abrupt interface is placed midway between two consecutive heterocationic planes. (c) Macroscopic averages of the electron density [$\bar{\bar{n}}(z)$] and electrostatic potential energy [$\bar{\bar{V}}(z)$]; the predictions of our model are also displayed.

responds to $\Delta\bar{n}(z)$, significantly different from zero or, equivalently, to nonconstant $\Delta\bar{V}(z)$. (ii) $\Delta\bar{n}(z)$ and $\Delta\bar{V}(z)$ are discontinuous at the interface and they are not physically linked to each other by a Poisson equation. (iii) The potential drop generated by $\Delta\bar{n}(z)$ (i.e., Δ_{dip} in the notation of Refs. 3 and 4) is only part of the total potential lineup Δ, the latter being recovered by addition of the difference Δ_{ref} between the average potentials of slabs of bulk materials. While Δ is a physically measurable property of the interface, its decomposition $\Delta = \Delta_{\mathrm{ref}} + \Delta_{\mathrm{dip}}$ bears no physical meaning since it depends on the arbitrary shape of the reference interface.[9] (iv) On the contrary, $\Delta\bar{V}(z)$ tends to different constant values on the two sides far from the interface whose difference is the potential lineup Δ if the arbitrary average values of the bulk Hartree potentials are aligned.[2]

We propose a new procedure to subtract bulk effects from $\bar{f}(z)$, which avoids the definition of an ideal interface and its use as a reference. In fact such a definition is unnecessary, arbitrary, and might lead one to erroneously attribute physical meaning to Δ_{dip}. We define the *macroscopic average* $\bar{\bar{f}}(z)$ as the one-dimensional average of $\bar{f}$ over a period centered at z: $\bar{\bar{f}}(z) = (1/a\int_{z-a/2}^{z+a/2}\bar{f}(s)\,ds$. This is equivalent to the three-dimensional average of $f(\mathbf{r})$ over a slab-adapted unit cell[9] centered at point $\mathbf{r}$ and therefore corresponds to the usual definition of macroscopic quantities in electrostatics. When applied to $\bar{n}(z)$ and to $\bar{V}(z)$, the construction gives functions $\bar{\bar{n}}(z)$ and $\bar{\bar{V}}(z)$ which have the following features: (i) They are continuous functions. (ii) They are derived from a single ground-state calculation and not from differences. (iii) In the two bulk regi5ns, $\bar{\bar{n}}(z)$ tends to a constant value n_0 (eight electrons per cell in our case), while $\bar{\bar{V}}(z)$ tends to constants differing by Δ. (iv) The interface region is unambiguously defined as the region where both $\bar{\bar{n}}(z)$ and $\bar{\bar{V}}(z)$ significantly deviate from constancy. (v) The density $\bar{\bar{n}}(z)$ is related to $\bar{\bar{V}}(z)$ by a one-dimensional Poisson equation and is a physically meaningful interface electron distribution, since $\bar{\bar{n}}(z) - n_0$ is the finite-range charge distribution which generates the interface macroscopic dipole. The above construction of $\bar{\bar{n}}(z)$ and $\bar{\bar{V}}(z)$ is based on the assumption that the interface is lattice matched. The concept of macroscopic average can, however, be extended to mismatched interfaces preserving all the above features (i)-(v).

In Fig. 1(c) we display $\bar{\bar{n}}(z)$ and $\bar{\bar{V}}(z)$ as obtained from first-principles calculations for the (111) interface. An inspection of Figs. 1(b) and 1(c) shows that our lattice is thick enough to satisfactorily reproduce bulk features midway between the two interfaces and that computational noise is small even on such a blown-up scale. Note that $\bar{\bar{n}}(z)$ has a typical dipolar shape around n_0 across the interface. The value of $\bar{\bar{V}}_{\mathrm{GaAs}} - \bar{\bar{V}}_{\mathrm{AlAs}}$ produced by this dipolar charge distribution is 0.41 eV. Despite large differences of $\bar{n}(z)$, calculations made for the (001) and (110) interfaces give similar shapes for $\bar{\bar{n}}(z)$ and $\bar{\bar{V}}(z)$ [see Figs. 1(c) and 2] and practically identical values for the lineups (0.41 and 0.43 eV, respectively). The (111) geometry deserves some further comments: While the two interfaces in our supercells are equivalent by symmetry for the (001) and (110) su-

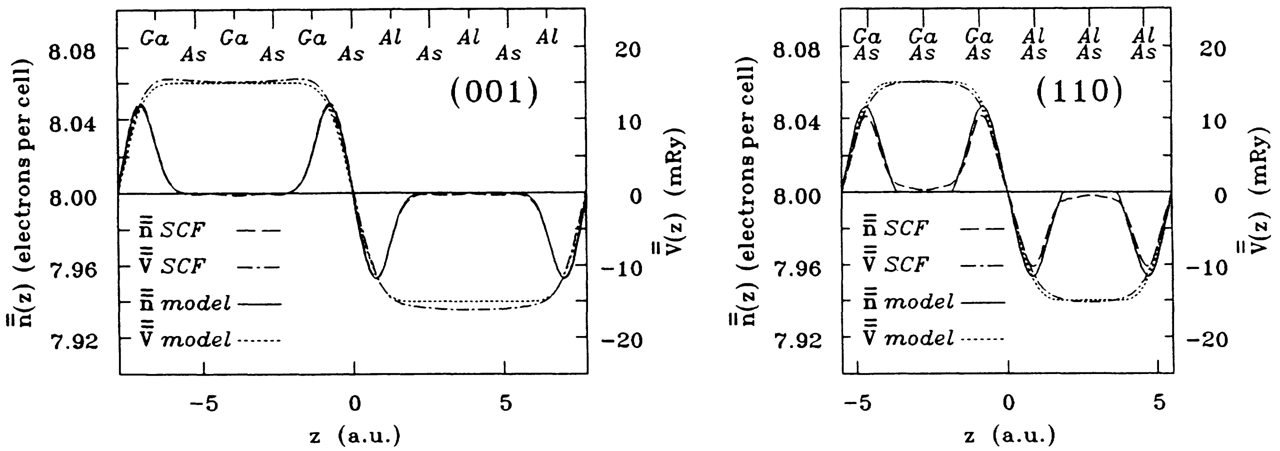

FIG. 2. Macroscopic averages of the first-principles (SCF) electron density [$\bar{\bar{n}}(z)$] and electrostatic potential energy [$\bar{\bar{V}}(z)$] of (GaAs)$_3$/(AlAs)$_3$ oriented along (001) and (110); the predictions of our model are also displayed.

perlattices, they are not for (111). In fact the two interfaces differ according to whether the interface bond which is parallel to the z direction is Ga-As or Al-As. The interface in the middle of Fig. 1 is of the former type (type A), while those at the figure borders are of the latter (type B). Type-A and type-B lineups can in principle be different ($\Delta_A \neq \Delta_B$), and net interfacial charges σ_A and σ_B can pile up; overall charge neutrality requires $\sigma_A = -\sigma_B$. The average electric field in the superlattice is determined by the overall boundary conditions and *not* by the local charge distribution; the use of periodic boundary conditions (as it is done here) amounts to the assumption of a zero average field, which physically corresponds to short circuiting the two free surfaces of a finite sample. The combined effect of $\Delta_A \neq \Delta_B$, $\sigma_A = -\sigma_B \neq 0$, and of the periodic boundary conditions results in nonvanishing slopes of the average electrostatic potentials in each of the bulklike regions. Analysis of the data presented in Fig. 1(c) gives $\Delta_B - \Delta_A = 0.07$ eV, and $\sigma_B = -\sigma_A = 2.8 \times 10^{-4}$ electrons per surface cell. A similar value (0.06 eV) for the difference in the two (111) lineups has been obtained by Muñoz, Sánchez-Dehesa, and Flores[14] after alignment of suitably defined midgap levels; our results differ from theirs in that they also obtain a sensible difference between the *average* (111) lineup and the lineups for the (001) and (110) interfaces.

The quantities calculated so far are electronic ground-state properties, therefore within the reach of our DFT calculation, the only essential approximation being LDA.[10] In principle, the same does not hold for band offsets, which also depend on bulk quasiparticle energies. However—as recent investigations[15] have shown that corrections to DFT-LDA are about the same for the two materials considered here—we decided to use LDA bulk energy bands to obtain valence-band offsets. The bulk band energies are defined to within the arbitrary constant discussed above[9]; when referring the band structure of each material to the average of its own electrostatic potential, the top of valence bands in GaAs is 0.05 eV higher than in AlAs. From addition of this quantity and spin-orbit effects (0.03 eV) to the potential lineups calculated above, we obtain for all the interfaces practically the same offset [average offset for (111)], i.e., 0.49–0.51 eV. This is in substantial agreement with the previous calculations for (001) and (110) offsets[3–5] and well within the present experimental error bar.[8]

The finding of an orientation-independent macroscopic dipole suggests the idea that for GaAs/AlAs the lineup is basically a bulk effect. Such independence is in fact obtained under the assumption that each of the two bulk solids is an assembly of elementary building blocks, and that these blocks can also be rigidly assembled to form an ideal reference interface. Starting from this reference, any orientation dependence can only be due to electronic redistributions at the interface. The orientation independence resulting from experimental data[7,8] and from our first-principles results indicates that a reference can be found which makes interface-specific relaxation phenomena negligibly small. A model where the elementary blocks are spherical atoms has been proposed by Van de Walle and Martin (VWM)[2]; it approximates the two bulk charge densities with a reasonable accuracy and gives a potential lineup of 0.60 eV.

We propose here a new model in which the building blocks are derived from the bulk charge densities of the constituents, using crystal symmetry. For lattice-matched common-anion heterojunctions, we decompose the bulk electronic densities into Wigner-Seitz cells (WSC) centered on the cations and with fractions of anions at four of the corners: They are neutral and by symmetry do not have dipole or quadrupole moments, i.e., the potential of WSC's is sufficiently short range not to produce macroscopic effects across the interface. Our model interface electronic density is then obtained simply by rigid juxtaposition of these WSC's; the total electronic charge is very much different for the four interfaces considered here, because of the geometry of each juxtaposition. Before averaging, the three-dimensional model electron density has small discontinuities at the boundaries of the WSC's at the interface, while the corresponding potential is continuous, showing an orientation-independent lineup of 0.41 eV, in agreement with the *ab initio* values reported above (0.41–0.43 eV).

Besides this single figure, the soundness of the physical picture underlying our model is best judged from an analysis of the predicted interface charge. To this end, we display in Figs. 1(c) and 2 the macroscopic averages of the electronic charge density and the electrostatic potential as predicted by the model for $(\mathrm{GaAs})_3/(\mathrm{AlAs})_3$ oriented along (111), (001), and (110). The agreement with first-principles calculations is extremely good. In particular the spatial extent of the interface regions and the shape of the dipolar charge distributions are well reproduced for all four interfaces. Of course, starting from the model, a small electronic rearrangement must occur in order to ensure at least charge continuity. Our results show that this rearrangement does not affect the total lineup for the (001) and (110) geometries, while it is responsible for the small lineup difference and interfacial charges in the case of the (111) orientation.

Our procedure has several advantages over the one of VWM's. It *exactly* reproduces the electronic density in the bulk, it provides a more accurate description of density profiles at the interface, and it yields a 0.49-eV valence-band offset which differs from our first-principles calculations by less than 0.02 eV, whereas VWM's model gives an error which is almost an order of magnitude larger. Of course, our model is less general than VWM in that in its present form it only applies to common-anion (or common-cation) lattice-matched heterojunctions. Extensions of this simple model to more general interfaces are possible and presently under study.[16]

We conclude by summarizing the main goals achieved in the present work. We have shown that an appropriate use of the basic concepts of electrostatics allows one to define an interface dipole at semiconductor interfaces avoiding any unnecessary reference to arbitrary ideal interfaces. Contrary to previous definitions, this dipole is directly related to the electrostatic potential lineup. We suggest that the arbitrariness in the definition of the reference interface can be removed by requesting that electronic relaxation with respect to it be a minimum. To this end we have introduced a new model which does make electronic redistribution at the interface negligibly small. The mere existence of such a model definitely rules out any significant role of interface-specific relaxation phenomena in this system. Finally, evidence has been given that a small difference exists between the lineups of the two inequivalent (111) interfaces which is associated with net interface charges and internal electric fields.

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