Comparison of Dipole Layers, Band Offsets, and Formation Enthalpies of GaAs-AlAs (110) and (001) Interfaces

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We report a very careful, self-consistent, relativistic pseudopotential calculation of the interfacial dipole double-layer potential, valence-band offset, and formation enthalpy of $(GaAs)_3(AlAs)_3(110)$. A comparison is made with identical calculations for the (001) superlattice with the following results [(001) in parentheses]: The interfacial dipole layer is 315 (154) meV. The formation enthalpy per twelve-atom unit cell is -21.9 $(+1.7)$ meV. The valence-band offset is (446) 447 meV. This lends credence to the idea that the band offset is a difference of bulk quantities and that vastly different interfaces set up whatever double layer is necessary to maintain that difference.

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The idea of effective midgap points (EMP) in semiconductors has recently become popular. To obtain the band offsets in a superlattice, one has merely to calculate the energy bands of the two constituents separately and line up their EMP. Although different workers[1,2] have defined the EMP somewhat differently, the concept is appealing and has met with some empirical success. One might raise the objection that the band offsets depend on the interfacial dipole double-layer potential Δ_{dip}, and that Δ_{dip} is strongly face dependent. One of the two major conclusions to be drawn from this work is that the Δ_{dip} of the (110) and (001) GaAs-AlAs interfaces differ by over a factor of 2 but that this difference exactly (to within our numerical accuracy) cancels a difference in the face dependence of the average Coulomb potential, leaving the band offsets face independent.

Recent calculations[3,4] of the formation enthalpy H of $(GaAs)_1(AlAs)_1(001)$ [5] have been positive, indicating that the interface is unstable to disproportionation, even at 0 K. Our very recent calculation[6] for $(GaAs)_3(AlAs_3)(001)$ found $H=0.6$ meV per interface (compared with 7.45 meV for the monolayer superlattices) indicating that the stability of the isolated (001) interface is too close to call. We here find $H=-10.95$ meV per interface for $(GaAs)_3(AlAs)_3(110)$, resulting in our second major conclusion: The isolated (110) interface is stable at 0 K.

Our computational method is identical to that described in I and will not be discussed except to question whether H for a twelve-atom unit cell can be calculated with millivolt accuracy. Systematic errors such as those inherent in the local-density approximation for exchange and correlation, the use of scalar relativistic pseudopotentials, and small (but identical) Gaussian basis sets cancel when the constituent semiconductor cohesive energies are subtracted from that of the superlattice. It is in real- and reciprocal-space integrations that large errors might arise. We here sample the six $\mathbf{k}$ points in the $\frac{1}{8}$ irreducible wedge of the Brillouin zone (BZ): $\mathbf{k}=(\pi/a)[\alpha(0,0,1)+\beta(1,\bar{1},0)+\frac{1}{6}(1,1,0)]$ with $\alpha=\frac{1}{4}$ and $\frac{3}{4}$, and $\beta=\frac{1}{6}$, $\frac{1}{2}$, and $\frac{5}{6}$. These represent 48 points in the full BZ and are equivalent to 144 points in the monolayer superlattice. We[3] sampled twelve $\mathbf{k}$ points in the $\frac{1}{16}$ wedge of the monolayer superlattice, representing 128 points in the full BZ. In I we made an eighteen-point wedge (192 full BZ) sample for the monolayer superlattice because it is equivalent to the six-point wedge sample of the three-layer (001) superlattice, and obtained a change of only 0.1 meV in the *total energy*. This BZ sampling lies between those two in density and should yield equally good results.[7] Our real-space integrations are performed with a fitting technique as described in I and Ref. 3. The 668 random points we generated for the zinc-blende unit cell become[8] 23 988 in the (110) superlattice; the fitting functions expand to 808 Gaussians and 900 symmetrized combinations of plane waves in this lower symmetry. It is very expensive to construct and manipulate the 1708×23 988 fitting matrices and so we did not compare different sets of random points. In I, where it was cheaper, we found a 16.9-meV variation in superlattice cohesive energy but only 1.0-meV variation in H due to random point selection which

TABLE I. Four contributions to the total energy and formation enthalpy of $(GaAs)_3(AlAs)_3(110)$ and (001) at a lattice constant $a=5.6622$ Å.

	(110)	(001)
$\sum_{nk}\epsilon_{nk}-\sum_{\mathbf{K}}V(\mathbf{K})\rho(\mathbf{K})$ (Ry)	23.501 380	23.495 903
$\frac{1}{2}\times 8\pi\Omega\sum_{\mathbf{K}}\rho^2(\mathbf{K})/K^2$ (Ry)	9.321 959	9.332 236
$\int[\epsilon_{xc}(\rho_T)\rho_T-\sum\epsilon_{xc}(\rho_c)\rho_c]$ (Ry)	−36.436 366	−36.439 433
E_{Ewald} (Ry)	−100.902 834	−100.902 834
E_{tot} (Ry)	−104.515 860	−104.514 128
E_{atom} (Ry)	−100.933 842	−100.933 842
E_{coh} (eV)	48.7334	48.7098
$3(E_{\mathrm{coh}}^{\mathrm{GaAs}}+E_{\mathrm{coh}}^{\mathrm{AlAs}})$ (eV)	48.7115	48.7115
Formation enthalpy (meV)	−21.9	1.7

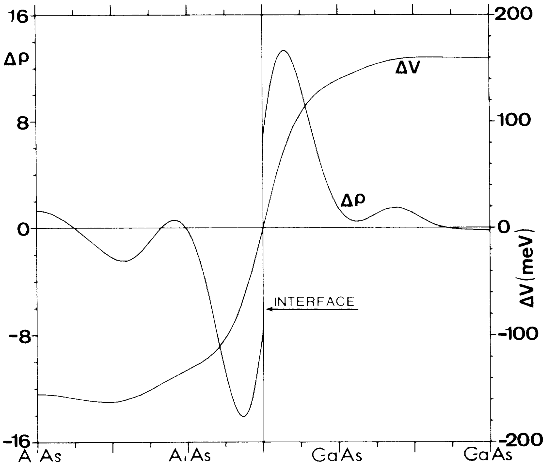

FIG. 1. Planar average of $\Delta\rho$ in units of 2.5×10^{-5} electron per cubic bohr and the double-layer potential ΔV it engenders. Here $\Delta\rho=\rho_{\mathrm{superlattice}}-\rho_{\mathrm{constituent}}$.

demonstrates the importance of using the same random points in the superlattice and zinc-blende crystals.[9] The fitting accuracy here is identical to that in I. One reason for this great accuracy is that Coulomb errors cancel to first order when the energy is calculated variationally.[10] We should also mention that our[6] GaAs and AlAs lattice constants are sufficiently close to experiment and to each other that strain effects in the superlattice are negligible.

Table I compares the four contributions to the cohesive energy and H with those for the (001) superlattice.[9] The Ewald energy, representing the interaction of point ions with a constant background of charge density, is identical in the two cases. The first term, representing kinetic and pseudopotential energy, and the exchange energy term are both more positive for (110) than (001), but the Coulomb-energy difference dominates and is less positive for (110) resulting[11] in a negative H. Most of this Coulomb-energy difference between three-layer (001) and (110) superlattices probably exists for isolated interfaces whereas the difference between one- and three-layer superlattices is attributed[6] to Coulomb repulsion between interfaces.

One might suspect that this energy difference is due to (001) being a polar interface while (110) is nonpolar; however, just completed calculations for the polar (111) interface yield $H_{(111)}=-20.8$ meV.

Figure 1 is a plot of the difference between the planar average of the superlattice charge density and that of its constituents and the potential ΔV that this double-layer charge distribution engenders. This net flow of charge from the Al to the Ga side is consistent with random-alloy nuclear resonance results[12] as well as with the larger binding energy[3] (i.e., the negative of E_{tot} displayed in Table I) of GaAs. The difference between ΔV at the central GaAs and AlAs planes (i.e., at the edges of the figure) is $\Delta_{\mathrm{dip}}=314.2$ meV. Note the large differences in both magnitude and shape between this and Fig. 3 of I. Note also that Δ_{dip} has not quite converged in cell thickness.[13] Figure 2 displays the planar average of the full crystal potential (except for the nonlocal part of the pseudopotential) with $\hat{V}$ the central

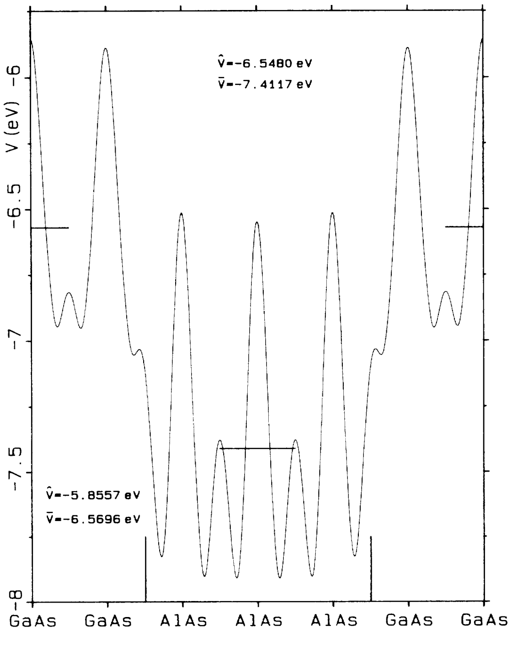

FIG. 2. Planar average of the local potential of the superlattice. The horizontal lines represent $\bar{V}$ which is V averaged over the central cells. $\hat{V}$ is V at the central GaAs and AlAs planes.

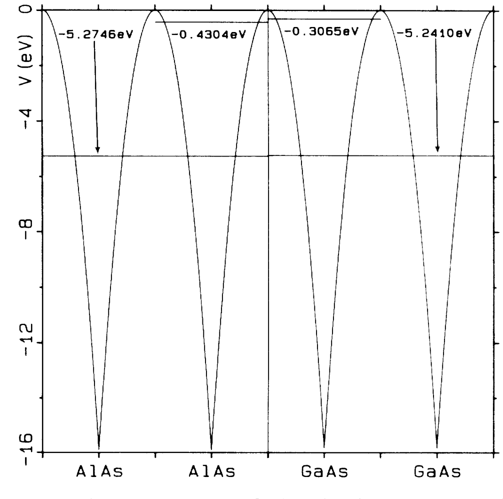

FIG. 3. Planar average of the Coulomb potential arising from point ions and bulk pseudocharge densities of GaAs and AlAs as described in the text. The long horizontal lines represent the average of these potentials. The shorter lines represent the tops of the valence bands with respect to these average potentials.

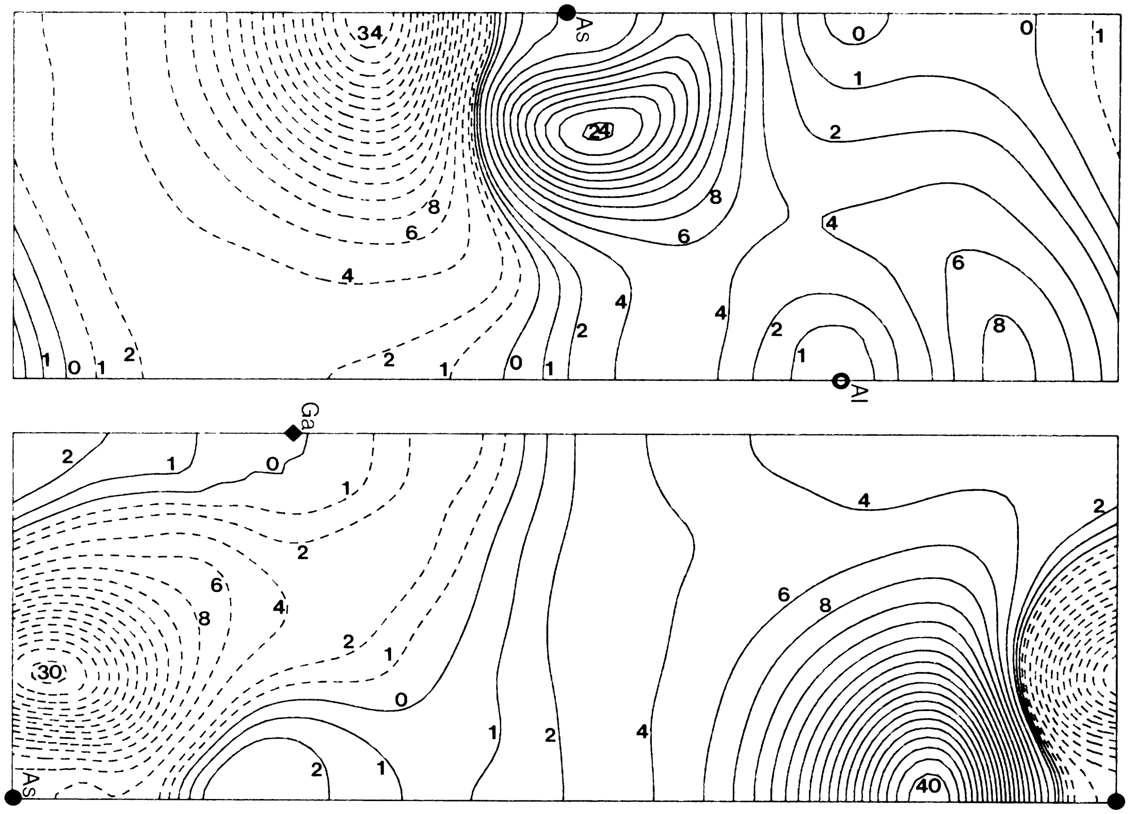

FIG. 4. Contour plots of $\Delta\rho$ in the two atomic planes on the either side of the interface, in units of Fig. 1. Solid lines represent positive $\Delta\rho$ and dashed lines negative $\Delta\rho$. A full unit cell is obtained by reflection of the plots in their long edges. Filled circles are As atoms, open circles are Al, and filled squares are Ga.

GaAs and AlAs plane potentials and $\bar{V}$ the average potential over the central cells. When the Γ_8 valence-band edges are calculated in the bulk crystals with respect to ΔV, the valence-band offset obtained is $\Delta E_V = 0.4444$ eV; when calculated with respect to $\Delta\bar{V}$, $\Delta E_V = 0.4494$ eV. We take the average, $\Delta E_V = 0.447$ eV, as our best estimate and compare it with our (001) result,[6] $\Delta E_V = 0.446$ eV. Equality of the (110) and (001) offsets to two decimal places has been found in accurate calculations[14] but not in more approximate ones.[15] The following calculation of ΔE_V is less accurate than our other two but is pedagogically useful.[16] In Fig. 3 we just juxtapose Coulomb potentials of (110) planar averaged slabs of bulk GaAs and AlAs charge densities. The $\Gamma_8^{(0)}$ levels are bulk values in which the arbitrary zero of Coulomb potential is taken to be the average slab potential. Figure 3 differs from Fig. 6 of I in sign[17] and in size of average potential discontinuity. Figure 3 differs from the superlattice planar averaged Coulomb potential by ΔV, the potential due to $\Delta\rho$, the charge which flows from AlAs to GaAs, shown in Fig. 1. Thus

$$\Delta E_V = \Gamma_8^{(0)}(\text{GaAs}) - \Gamma_8^{(0)}(\text{AlAs}) + \Delta_{\text{dip}} = -0.3065 + 0.4304 + 0.3142\ \text{eV} = 0.438\ \text{eV}.$$

Here we see how the arbitrary zero of bulk Coulomb potential becomes well defined by slicing of the bulk into slabs[18] and how the facial dependence of its discontinuity between GaAs and AlAs slabs is canceled by the facial dependence of Δ_{dip}. This cancellation is obviously not universal as work functions are face dependent.[19]

Figure 4 displays contour plots of the difference between the superlattice and bulk semiconductor charge densities $\Delta\rho$, in the two atomic planes on either side of (and parallel to) the interface.[20] In Fig. 1 we see that the AlAs plane sits almost exactly on a node of the planar average of $\Delta\rho$, but $\Delta\rho$ itself is still quite large. This figure is remarkably similar to Fig. 2 of I when one considers that there the As atoms are at the interface and the contours lie in a plane intersecting the interface. In both figures, most of the action is around the As atoms. On the GaAs side, charge flows from the bonding direction to a direction pointing away from Ga atoms in the plane; the opposite flow occurs on the AlAs side.

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[1] J. Tersoff, Phys. Rev. B **30**, 4874 (1984), and Surf. Sci. **168**, 275 (1986).

[2] M. Cardona and N. E. Christensen, Phys. Rev. B **35**, 6182 (1987).

[3] D. M. Bylander and L. Kleinman, Phys. Rev. B **34**, 5280 (1986).

[4] D. M. Wood, S.-H. Wei, and A. Zunger, Phys. Rev. Lett. **58**, 1123 (1987).

[5] The (011) and (100) monolayer superlattices are identical, differing only by a 90° rotation of their unit cells.

[6] D. M. Bylander and L. Kleinman, Phys. Rev. B **36**, 1775 (1987), hereafter called I.

[7] We estimate an uncertainty of 0.3 meV for the three-layer superlattice energies due to the finite sampling of the BZ, i.e., three times larger than for the monolayer superlattice.

[8] In each zinc-blende cell we have 96 points on a radial mesh at random angles about each atom plus one at the atom plus 474 random points throughout the cell. The 24 zinc-blende symmetrically equivalent points represented by one random point are represented by six inequivalent points in the (110) superlattice symmetry. Also each superlattice unit cell contains six zinc-blende cells. Thus $N=36(2\times96+474)+12=23\,988$.

[9] The set of random points used here corresponds to set I in I. This set gave the largest cohesive energies and, although there is no variational principle, we generally find that the better the fit, the larger the cohesive energy.

[10] We subtract the electron-electron contribution from the sum of one-electron eigenvalues and add its energy. For the Coulomb terms this gives $-V_{\mathrm{Coul}}\rho_{\mathrm{out}}+\frac{1}{2}\sum_{\mathbf{k}}4\pi\rho_{\mathrm{out}}^2(\mathbf{K})/K^2$ where V_{Coul} is the exact input potential to the final iteration (it should contain whatever errors are in that input potential). Writing $\rho_{\mathrm{out}}=\rho_0+\delta$ we have

$$-\sum_{\mathbf{k}}4\pi[\rho_{\mathrm{in}}(\mathbf{K})\rho_{\mathrm{out}}(K)-\tfrac{1}{2}\rho_{\mathrm{out}}^2(\mathbf{K})]/K^2=-\sum_{\mathbf{k}}4\pi\{\rho_{\mathrm{in}}(\mathbf{K})\rho_0(\mathbf{K})-\tfrac{1}{2}\rho_0^2(\mathbf{K})+[\rho_{\mathrm{in}}(\mathbf{K})-\rho_0(\mathbf{K})]\delta_{\mathbf{K}}-\tfrac{1}{2}\delta_{\mathbf{K}}^2\}/K^2.$$

The first two terms are exact while the last two are second order in $\delta_{\mathbf{K}}$.

[11] The formation enthalpy per interface is half that per unit cell.

[12] K. Akimoto, Y. Mori, and C. Kojima, Phys. Rev. B **35**, 3799 (1987).

[13] This unit cell is thinner by a factor of $2^{-1/2}$ than the (001) which accounts for the poorer convergence.

[14] C. G. Van de Walle and R. M. Martin, in *Computer-Based Microscopic Description of the Structure and Properties of Materials,* edited by J. Broughton, W. Krakow, and S. T. Pantelides, MRS Symposia Proceedings No. 63 (Materials Research Society, Pittsburgh, 1986).

[15] A. Muñoz, J. Sánchez-Dehesa, and F. Flores, Phys. Rev. B **35**, 6468 (1987).

[16] Because neither the exchange correlation nor Coulomb potentials have converged as a function of cell thickness and Δ_{dip} is a response of the system to the full potential, ΔE_V calculated from Fig. 2 is more accurate than from Fig. 3. In the more converged (001) case all three values were within 0.9 meV.

[17] The sign reversal occurs because the (001) slabs are cut through As planes, whereas the (110) are cut between atomic planes.

[18] L. Kleinman, Phys. Rev. B **24**, 7412 (1981).

[19] If one considers the superlattice to be a long-wavelength perturbation of the virtual crystal, linear-response theory indicates that the self-consistent potential is, at most, weakly dependent on the direction of the wave vector. The vacuum interface is too strong a perturbation for linear theory to apply.

[20] In I these plots are in planes intersecting the interface. But here the interface bisects covalent bonds, and it is not very informative to subtract the GaAs charge density from one half of a bond and the AlAs charge density from the other.