Large interfacial charge density in unstrained GaAs-AlAs(111) superlattices

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We calculate the formation enthalpy of $(GaAs)_n(AlAs)_n(111)$ superlattices for $n=1$ and 3 and compare with previous (001) and (110) calculations. The (111) interfacial double layer and valence-band offsets for $n=3$ are also compared with (001) and (110) calculations. A new feature of the (111) unstrained superlattice is large zeroth-order internal electric fields which set up large interfacial charge densities ($\sim\pm 4.3\times 10^{-2}$ C/m^2) whose fields very nearly exactly cancel the zeroth-order fields.

In previous work [hereafter I (Ref. 1) and II (Ref. 2)] we compared the interfacial double layers, formation enthalpies, and valence-band offsets of $(GaAs)_n(AlAs)_n(001)$ and (110) superlattices with $n=1$ and 3. In calculating these quantities for (111) superlattices we find unexpectedly large zeroth-order electric fields across the quantum wells and very large net electric charges on the interfaces which set up screening fields. These can arise because the unstrained[3] (111) superlattice has the same symmetry as the piezoelectrically strained bulk zinc-blende crystal.

The computational method is well described in I and II where we claimed relative accuracies of a few meV. We use the same Gaussian basis set here. We fit charge densities, potentials, and energy densities with the same mixed set of functions (in, of course, different symmetrized combinations) at a set of superlattice random points generated from the same seminal zinc-blende set.[4] The only part of the calculation in which there is not an exact one-to-one correspondence among (001), (110), and (111) is the **k**-point sample of the Brillouin zone (BZ). For $(GaAs)_3(AlAs)_3(111)$ we use a 108-point BZ sample[5] which is considerably denser and thus even more accurate than the 64- and 48-point (001) and (110) samples. This configuration is used to calculate the cohesive energy of the monolayer (111) superlattice and bulk GaAs and AlAs as well. Thus the small lack of convergence in the BZ sum cancels on subtracting the bulk energies from the superlattice energy to obtain the formation enthalpy.

There are two different (111) interfaces. The interfacial planes are As planes where each As atom has three Ga neighbors and one Al neighbor (a Ga interface) or three Al neighbors and one Ga (an Al interface). The formation enthalpy of the Ga and Al interfaces cannot be calculated separately since they always occur together in the superlattice. One could consider a slab with a single interface and two surfaces. If one had a Ga (Al) interface, one surface plane would consist of As atoms on the AlAs (GaAs) side and the other surface plane would consist of Ga (Al) atoms. Thus the enthalpy of the two different interfaces cannot be disentangled from the surface energy of the four different kinds of surfaces.[6] Because the interfaces have equal and opposite charges in the superlattice, we must assume that they are also charged in the slab and that this charge comes from the surfaces so that the surfaces cannot be ignored by considering the interface to lie between two semi-infinite bulk crystals.

In Table I we list the contributions to the total and cohesive energies and formation enthalpy of the one[7]- and three-layer (111) superlattices, and in Table II we compare the formation enthalpy per unit cell (i.e., per pair of interfaces) for the (001), (110), and (111) one- and three-layer superlattices.[8] We can see that the[9] $(GaAs)_1(AlAs)_1(001)$-(110) and (111) superlattices are unstable to disproportionation, that $(GaAs)_3(AlAs)_3(001)$ is almost stable while $(GaAs)_3(AlAs)_3(111)$ and (110) are, re-

TABLE I. Four contributions to the total and cohesive energies and formation enthalpy of $3(GaAs)_1(AlAs)_1(111)$ and $(GaAs)_3(AlAs)_3(111)$ at lattice constant $a=5.6622$ Å.

	$n=1$	$n=3$
$\sum_{n,\mathbf{k}}\epsilon_{n,\mathbf{k}}-\sum_{\mathbf{K}}V(K)\rho(K)$ (Ry)	23.497 231	23.497 679
$(\frac{1}{2})8\pi\Omega\sum_K\rho^2(K)/K^2$ (Ry)	9.330 470	9.330 278
$\int\left[\epsilon_{xc}(\rho_T)\rho_T-\sum\epsilon_{xc}(\rho_C)\rho_C\right]$ (Ry)	−36.438 163	−36.439 803
E_{Ewald} (Ry)	−100.902 834	−100.902 834
E_{total} (Ry)	−104.513 296	−104.514 680
E_{atom} (Ry)	−100.933 842	−100.933 842
E_{coh} (eV)	48.6985	48.7173
$3(E^{\text{GaAs}}+E^{\text{AlAs}})$ (eV)	48.7289	48.7289
Formation enthalpy (meV)	30.4	11.6

TABLE II. Formation enthalpy (in meV) per unit cell (i.e., per pair of interfaces) for $n=1$ and $n=3$ $(GaAs)_n(AlAs)_n$(001), (110), and (111) superlattices.

	(001)	(110)	(111)
$n=1$	15.1	14.9	10.1
$n=3$	1.7	27.8	11.6

spectively, slightly and much more unstable than the monolayer superlattices (per unit cell or per interface; not per atom). This is consistent with the fact that (001) superlattices are easiest to grow and (110) hardest. Note also that the polar interfaces are more stable than the nonpolar (110).

In Figure 1 we plot the planar average of the total (excluding the nonlocal part) superlattice pseudopotential. The Γ_8 levels calculated in AlAs and GaAs with respect to $\bar{V}$ or $\hat{V}$ result in valence-band offsets of $\Delta E_V=442.0$ and 442.9 meV. Here $\hat{V}$ and $\bar{V}$ are the planar averaged potential at the well centers and averaged over the well central cells. A few workers[10,11] calculate different offsets at the Ga and Al interfaces. Note that if one calculates the offest from well center to well center, the periodicity of the superlattice forces the offsets to be identical. One could try the calculation with slabs containing a single interface but in that case there will be long-range electric fields and the four surfaces will have different work functions. The separation of the two work functions from the band offset in a slab with an internal electric field does not seem to be unique.

In Fig. 2 we display $\Delta\rho$ and ΔV,[12] the potential it induces. $\Delta\rho$ is the planar average of the superlattice electric charge density minus that of its constituents. The interfacial double-layer nature of this charge density which was so obvious in I and II is obscured by the large peaks. The double-layer potential Δ_{dip} is obtained from ΔV which was arbitrarily zeroed at the center of GaAs wells and takes the value -0.2525 eV at the center of the AlAs wells. In Table III we compare the (001), (110), and (111) Δ_{dip}, ΔE_V, and δ, the difference between ΔE_V obtained from $\bar{V}$ and $\hat{V}$. As the wells get thicker δ must vanish and we note that the three-layer (111), (001), and (110) thicknesses are in a $2/\sqrt{3}:1:1/\sqrt{2}$ ratio. As discussed in II, the different Δ_{dip} are necessary to obtain the near identity of the ΔE_V which is even more marked than that found by van de Walle and Martin.[13]

The Coulomb potential due to the planar averaged charge density is given by

$$V(z)=V(0)+z\left[\frac{\partial V}{\partial z}\right]_0-4\pi\int_0^z dz'\int_0^{z'}\rho(z'')dz'' \ . \tag{1}$$

In I and II $(\partial V/\partial z)_0$ was zero by symmetry but here it must (unless one wants to assume an externally applied electric field) be chosen to ensure periodicity. In Fig. 3 we plot the potential due to a superlattice made up of alternating bulk GaAs and AlAs(111) slab charge densities. Had $(\partial V/\partial z)_0$ been taken to be zero, the potential rise across the GaAs (from plane G_0 to plane A_0) would have been 58.7729 V and across the AlAs (from A_0 to G_0) would have been 63.5023 V. This on the average is canceled by $(\partial V/\partial z)_0$, leaving a linear rise from A_0 to A_1 to

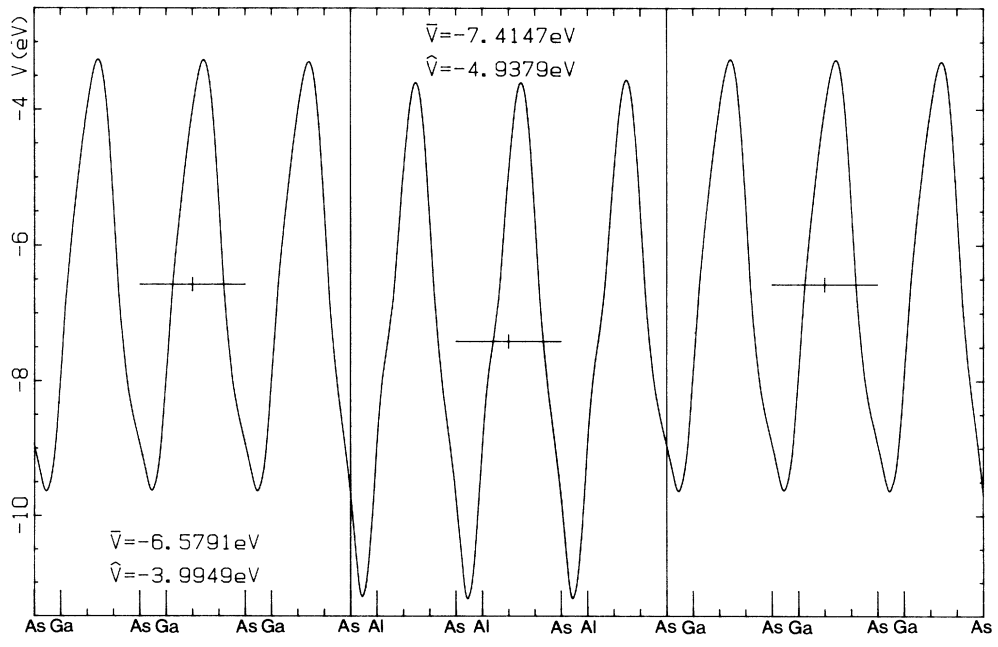

FIG. 1. Planar average of the self-consistent pseudopotential (not including the nonlocal part) of $(GaAs)_3(AlAs)_3(111)$. The atomic planes are denoted by large tick marks and the interfacial planes by vertical lines. The horizontal lines represent $\bar{V}$ and run the width of the central cell over which $\bar{V}$ is obtained. $\hat{V}$ is the potential at the vertical mark in the center of the central cell.

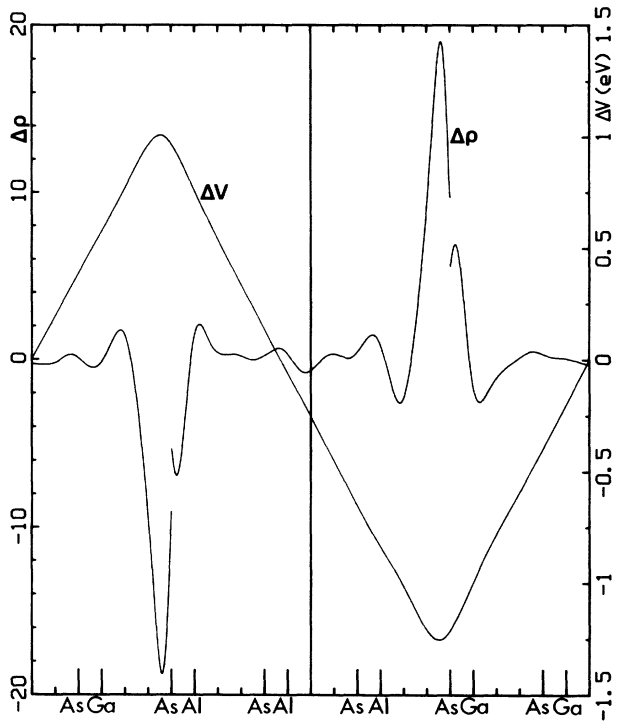

FIG. 2. Plot of $\Delta\rho$, the planar average of the difference between the superlattice charge density and that of bulk GaAs and AlAs in their respective quantum wells, in units of 2.5×10^{-5} electrons per cubic bohr. The discontinuities in $\Delta\rho$ occur at the interfacial planes. The potential induced by $\Delta\rho$ is ΔV which is arbitrarily zeroed at the center of the GaAs well.

A_2 to G_0 of 2.3647 V and the same linear drop from G_0 to G_1 to G_2 to A_0. This represents electric fields of $\pm2.411\times10^9$ V/m. These, of course, cannot be sustained by the superlattice and its charge density differs from this slab model by $\Delta\rho$ in Fig. 2. The sharp positive and negative peaks in $\Delta\rho$ at the interface give rise to screening electric fields. When ΔV is added to the slab potential, the potential given by the lower curve in Fig. 3 is obtained. There still remains a potential increase[14] of 3.3 meV from A_1 to A_2 and a decrease of 6.4 meV from G_1 to G_2, corresponding to electric fields of 1.01×10^7 and -1.96×10^7 V/m. If one integrates $\Delta\rho$ between G_2 and A_1 (A_2 and G_1) to obtain the net charge on the Al (Ga) interface one finds $-0.036\,92e/a$ ($0.036\,85e/a$). If one integrates from cell center to cell center, $\pm0.037\,176e/a$ is obtained. Here $a=13.88$ Å^2 is the interfacial unit-cell area. Now $0.037\,176e/a=4.291\times10^{-2}$ C/m^2 which yields $E=\sigma/2\epsilon_0=2.423\times10^9$ V/m. We can ask the question, suppose the quantum wells were sufficiently thick that there was a central region of each well in which $\Delta\rho=0$, would there exist electric fields across the central regions? (We expect that $\Delta\rho$ decays exponentially away from the interfaces.) In the three-layer film we found fields that were less than 1% of the zeroth-order fields across the central cells of the wells but when we calculated a screening field due to the integrated charge density between well centers, we found it approximately $\frac{1}{2}$% larger than the zeroth-order field. Thus since we have two estimates of opposite sign for the electric field in the central region of the thicker wells, we must assume that the actual field is an extremely small fraction of the zeroth-order field. On the other hand, there is no symmetry requirement that the field vanish and that which is not forbidden by symmetry usually exists. What is interesting is not that the field exists but that it is so small relative to the field in our zeroth-order model of alternating bulk slabs. While that model is unphysical at the interfaces (the charge density is discontinuous, for instance), any model, which is electrically neutral at the interfaces and bulklike in the middle of the quantum wells,

TABLE III. Interfacial double layers Δ_{dip} and valence-band offsets ΔE_V (in meV) for $(GaAs)_3(AlAs)_3$(001), (110), and (111). $\delta/2$ represents an uncertainty in ΔE_V.

	(001)	(110)	(111)
Δ_{dip}	154	314	254
ΔE_V	446	447	442
δ	−0.9	5.0	0.9

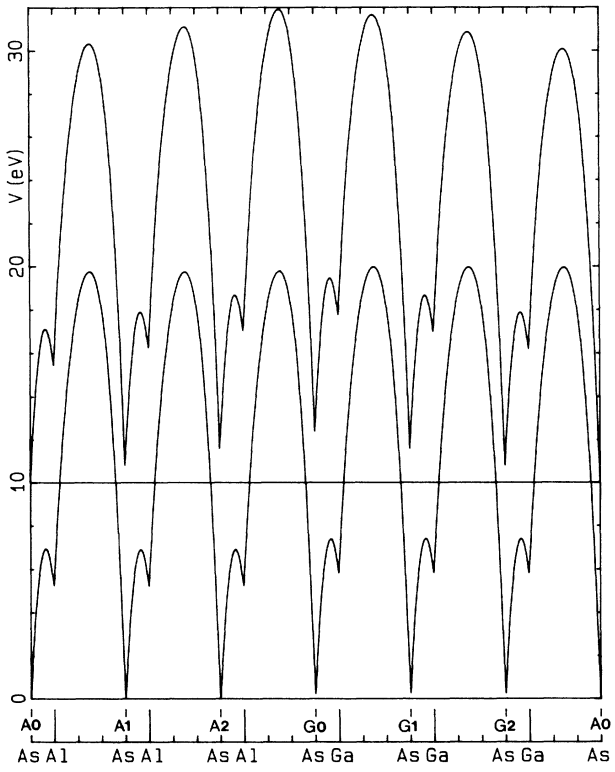

FIG. 3. The planar average of the Coulomb potential of adjacent three-layer (111) slabs of bulk GaAs and AlAs charge densities calculated from Eq. (1) with $(\partial V/\partial z)_0$ chosen to make the potential periodic (upper curve). The lower curve is the sum of the upper curve plus ΔV of Fig. 2. The zeros of both curves are arbitrary. The As planes are labeled for easy reference in the text.

will yield exactly the same fields in its bulklike regions.[15]

One might have supposed as Mailhiot and Smith[16] (MS) did when considering piezoelectric fields in strained, i.e., lattice-mismatched, (111) superlattices that long-range electric fields are screened by the dielectric constants of the constituent semiconductors. The unscreened piezoelectric fields are, even for 1.5% strains, only about 10% of the zeroth-order fields we are concerned with and are not distinguishable from them, in the sense that once the cubic symmetry is destroyed by picking out one of the [111] directions, other changes which do not further reduce the symmetry add nothing basically new. Because in the unstrained superlattice all atoms except those at the interface remain in tetrahedral atomic surroundings, there is a physical difference between the two cases. Thus it is quite possible that the MS prescription for obtaining the piezoelectric fields is essentially correct[17] but that internal fields in unstrained slabs are almost completely screened. MS have pointed out that internal electric fields reduce energy-band gaps. The detection of reduced gaps would be one way to prove the existence of such fields.

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[1]D. M. Bylander and L. Kleinman, Phys. Rev. B **36**, 3229 (1987).

[2]D. M. Bylander and L. Kleinman, Phys. Rev. Lett. **59**, 2091 (1987); **60**, 472(E) (1988).

[3]Our calculated, as well as the experimental, bulk GaAs and AlAs lattice constants are sufficiently close to one another that negligible error is made by assuming a zinc-blende lattice with the average calculated lattice constant for the superlattice.

[4]We fit with 732 symmetrized Gaussian and 665 symmetrized plane-wave combinations at 15 996 random points in the three-layer (111) superlattice.

[5]The twelve $\mathbf{k}$ points in the $\frac{1}{12}$ irreducible wedge of the BZ are $\mathbf{k}=(2\pi/a)[\frac{1}{24}(1,1,1)+(i/9)(1,\bar{1},0)+(j/27)(1,1,\bar{2})]$ with $(i,j)=(1,\pm1),(3,\pm1),(5,\pm1),(2,\pm2),(4,\pm2),(4,\pm4)$.

[6]The two interfaces and four surfaces present six unknown energies but there are only five calculations that can be made. These are superlattice, GaAs and AlAs slabs, and slabs with either a Ga or Al interface.

[7]Because the monolayer superlattice is not commensurate with the three-layer repeat distance of the fcc lattice in the [111] direction, we chose a unit cell containing three monolayers. There is a unit cell containing one monolayer but our computer programs are not set up for that symmetry. The direct gap at Γ in the monolayer superlattice [to which the tetrahedral Γ and L $(\frac{1}{2},\frac{1}{2},\frac{1}{2})$ points project] is 0.898 eV. Because they differ by a $(\frac{1}{2},\frac{1}{2},\frac{1}{2})$ reciprocal-lattice vector of the superlattice, X (1,0,0) and L $(\frac{1}{2},\frac{\bar{1}}{2},\frac{\bar{1}}{2})$ project to the same superlattice BZ point. The indirect gap to this point is 1.228 eV. Thus unlike $(GaAs)_1(AlAs)_1(001)$, $(GaAs)_1(AlAs)_1(111)$ is a direct-gap semiconductor.

[8]In I we checked the fitting accuracy by using two different sets of random points. The results for the first set, which corresponds to the set used in II and here, are the ones quoted here. The second set resulted in a 1-meV reduction of the $(GaAs)_3(AlAs)_3$ (001) formation enthalpy and had no effect on the band offset.

[9]The (001) and (110) monolayer superlattices are identical for a 90° rotation. The tiny difference seen in Table II, which arises from the different (001) and (110) BZ samples, gives an indication of the accuracy of these calculations.

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

[11]B. Haussy, C. Priester, G. Allan, and M. Lannoo, Phys. Rev. B **36**, 1105 (1987).

[12]Unlike the corresponding plots in I and II, we here include the negative sign of the electron in $\Delta\rho$ so that its peaks will not overlap those of ΔV.

[13]C. G. van de Walle and R. M. Martin, J. Vac. Sci. Technol. B **4**, 1055 (1986).

[14]The potentials at planes A_0, A_1, A_2, G_0, G_1, and G_2 are 0, -0.0430, -0.0398, 0.1902, 0.2137, and 0.2073 eV. The G_1-A_1 potential difference is approximately equal to Δ_{dip}.

[15]One can find a pair of planes such that the zeroth-order model will have no electric field (even if piezoelectric fields are present) but our interfacial planes are the only physically reasonable ones because they separate regions containing GaAs bonds from those containing AlAs bonds. The calculated interfacial charge varies so that the zeroth-order model field plus screening field is independent of where the interface is chosen.

[16]C. Mailhiot and D. L. Smith, Phys. Rev. B **35**, 1242 (1987).

[17]These strains do not destroy the superlattice periodicity. To give that periodicity to the piezoelectric field one must in general add a constant field to the MS field. See Eq. (1).