PHYSICAL REVIEW B VOLUME 41, NUMBER 6 15 FEBRUARY 1990-II

Huge electric fields in Ge/GaAs (001) and (111) superlattices and their effect on interfacial stability

D. M. Bylander and Leonard Kleinman
Department of Physics, University of Texas, Austin, Texas 78712-1081
(Received 24 May 1989)

Self-consistent relativistic pseudopotential calculations of $Ge_6/(GaAs)_3$ (001) and (111) superlattices yield a sawtooth potential resulting in electric fields of magnitude 10^9 V/m. This has little effect on the (111) energy bands but localized states on the two (001) interfaces are shifted in opposite directions, resulting in a negative energy gap. Formation-enthalpy calculations indicate the (111) interface is probably stable against reconstruction while the (001) interface is probably unstable.

The imposition of periodic boundary conditions precludes the possibility of constant electric fields in semiconductors. However, in superlattices a sawtoothlike potential with the periodicity of the superlattice may arise which will result in electric fields of alternating sign in the two quantum wells. These fields are symmetry allowed, and thus expected to occur, whenever there is no symmetry operation which interchanges the two interfaces. Thus, for the zinc-blende structure (where one of the two constituents may be diamond structure) they are always expected for (111) superlattices and in the (001) case when the two constituents have no common ion. [For example, for every symmetry operation in $(Ge)_6/(GaAs)_3$ (001), there are two operations in $(AlAs)_3/(GaAs)_3$ (001), one of which involves a twofold (100) rotation which interchanges the two identical As interfacial planes.] Mailhiot and Smith[1] (MS) have calculated piezoelectric fields in strained (i.e., lattice-mismatched) (111) superlattices. The piezoelectric fields are a contribution to the alternating fields which arise from inner displacements of the sublattices with (111) strains and may add or subtract from the fields that would be present in the absence of inner displacements. The important nonlinear optical effects discussed by MS do not, of course, depend on the source of the field. We[2] recently considered $(GaAs)_3/(AlAs)_3$ (111). A model superlattice consisting of alternating slabs of bulk GaAs and AlAs charge densities resulted in fields of $\pm 2.41\times 10^9$ V/m, but in the self-consistent superlattice, those fields were more than 100 times smaller.[3] We attribute the relative smallness of these fields to the similarity of GaAs and AlAs as exemplified by the very small interfacial formation enthalpy [11.6 meV per pair of (111) interfaces]. We[4] recently calculated the interfacial formation enthalpy of $(GaAs)_3/Ge_6$ (110) to be 390 meV. This suggests that the polar interfaces of this system might give rise to large electric fields.

As far as we know there are four[5-8] previous calculations for GaAs/Ge (111), while the GaAs/Ge (001) interfaces have been studied by Baraff, Appelbaum, and Hamann (BAH) (Ref. 9) and by Pollman and Pantelides (PP).[10] Except for BAH, all used non-self-consistent tight-binding methods of varying degrees of sophistication, but which do not allow for the possibility of electric fields. BAH treated three layers of one constituent grown epitaxially on a semi-infinite crystal of the other. They did not allow an electric field in the semi-infinite constituent and effectively quenched the field in the other constituent by saturating the surface dangling bonds with hydrogen and by choosing the Fermi level to yield a $\frac{3}{4}$ filling of the Ge-Ga interface band[11] in spite of the top of the Ge valence band being above this E_F. Nevertheless, others[12,13] have noted that electric fields must be present and have asserted, we believe incorrectly, that both these interfaces must reconstruct in order to eliminate the fields.

We assume unstrained $(GaAs)_3/Ge_6$ (001) and (111) superlattices with the zinc-blende lattice constant $a_0 = 10.6998$ bohrs, the average of our[4] calculated Ge and GaAs lattice constants. Our calculated lattice mismatch was 0.0146 Å compared with the experimental 0.005 Å so that had we allowed (111) strains, the calculated piezoelectric contribution to the field would have been three times larger than its actual negligible value. We use the same relativistic norm-conserving pseudopotential and expand in the same set of Gaussians that we used[4] for $(GaAs)_3/Ge_6$ (110). The Brillouin-zone (BZ) points sampled are identical to those sampled for $(GaAs)_3/(AlAs)_3$ (001) (Ref. 14) and (111) (Ref. 2) except that, as a consequence of having half the symmetry, the (001) BZ irreducible wedge is twice as large here.[15] We sample the 24 lowest bands at each point of the BZ to attain a self-consistency of 2 meV between input and output potentials. Since the (001) superlattice has a negative energy gap, that calculation is not truly self-consistent.[16] Because its bands are wildly dispersive, an accurate calculation would require an extremely fine mesh of BZ points. Noting that the well-known band-gap error due to the use of an exchange-correlation density functional is 0.65 eV or larger[17] so that conduction- and valence-band states will be misordered in any case, we felt the tedious fully self-consistent calculation was not justified.

We define the electric field $E(\zeta)$, where ζ is the normal coordinate, to be[18]

$$E(\zeta)=[V_0(\zeta+\tfrac{1}{2}d)-V_0(\zeta-\tfrac{1}{2}d)]/d \ , \qquad (1)$$

where V_0 is the planar average of the Coulomb potential, and d is the fcc interplanar separation, i.e., $d_{(001)}=a_0/2$ and $d_{(111)}=a_0/\sqrt{3}$. These fields are plotted in Fig. 1 and Fig. 2, and their values at the point midway between the

 ©1990 The American Physical Society

central atomic planes of each quantum well are listed in Table I along with the interfacial formation enthalpy H, calculated in the usual manner.[14,19] These fields are 2 orders of magnitude larger than the 100-kV/cm piezoelectric fields occurring with a 1.5% lattice mismatch.[1] Note that the (001) field lines run from the Ga to the As interface, while the (111) field runs oppositely. The direction of the (001) field is determined by the interface states which are holes on the Ga and electrons on the As interface, whereas the (111) field direction is more subtle. Overly simple arguments of Harrison *et al.*[13] which neglect interface states predict that the field lines run from the As to the Ga interface in both cases.

The potential seen by Ge—Ga bonds is less attractive than that seen by either Ge—Ge or Ga—As bonds. Thus, valence-band states on this interface are pushed above the Fermi energy. Similarly, Ge—As bonds see a more attractive potential than Ge—Ge or Ga—As bonds, and conduction-band states are pulled below the Fermi energy on this interface. Because the Ge-Ga and Ge-As separations are $\sqrt{3}$ times larger in the (111) case, the perturbation is too weak there to create localized interface states. The holes on the Ge—Ga bonds are very strongly localized for $\mathbf{k}=(\alpha,\alpha,\beta)$ which can be understood as follows. Since we have six zinc-blende unit cells per superlattice cell, we expect six s electrons and eighteen p electrons (neglecting spin) in the valence bands. s, p_x+p_y, and p_z are even under reflection in the plane of $\mathbf{k}$ and transform with $\bar{\Delta}_1$ symmetry while p_x-p_y is odd and $\bar{\Delta}_2$. We find that the 19th $\bar{\Delta}_1$ band crosses the sixth $\bar{\Delta}_2$ band several times. Note $\mathbf{k}=(\alpha,-\alpha,\beta)$ is not equivalent to (α,α,β) and has a large gap between the 24th and 25th bands. The Ge—Ga bonds point in $[1,\bar{1},1]$ and $[\bar{1},1,1]$ directions where $x-y$ is maximal but the bonds between planes on either side of the interface point in $[111]$ and $[\bar{1}\bar{1}1]$ directions where $x-y$ vanishes. Thus, for $\bar{\Delta}_2$, the interface bonds are effectively decoupled from neighboring bonds. The $\bar{\Delta}_1^{19}$ As-Ge interface states have strong s-p hybridization and are more diffuse. Note that were we to apply a gap correction, raising the $\bar{\Delta}_1^{19}$ band, we would depopulate As and populate Ga interface states which

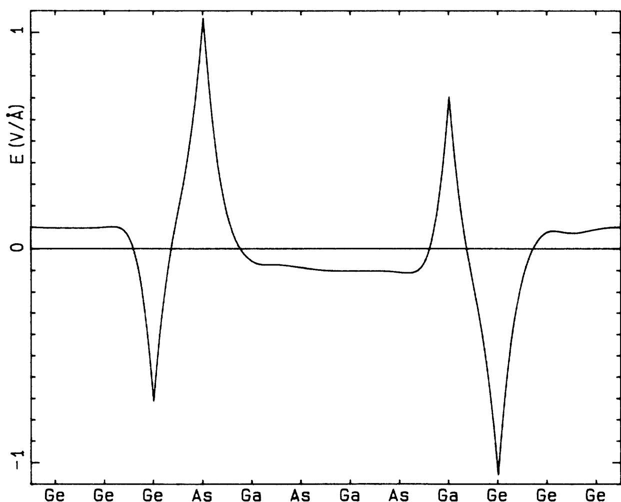

FIG. 1. Electric field in a $(Ge)_6/(GaAs)_3$ (001) superlattice. A positive E means the field lines run from left to right.

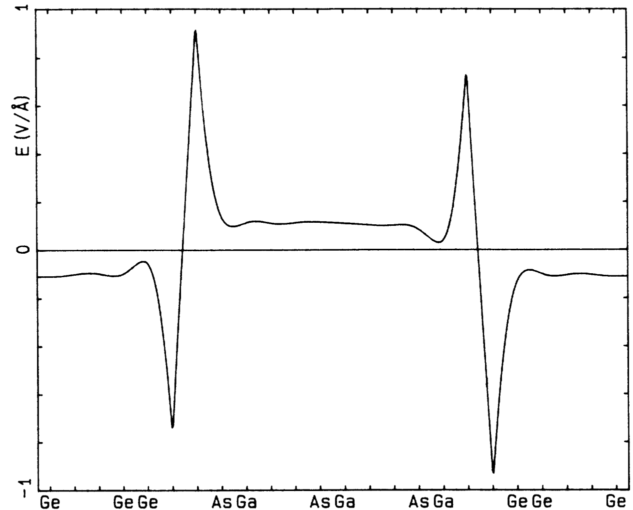

FIG. 2. Electric field in a $(Ge_6)/(GaAs)_3$ (111) superlattice. A positive E means the field lines run from left to right.

would decrease the electric field which would oppose the raising of $\bar{\Delta}_1^{19}$ relative to $\bar{\Delta}_2^{6}$. Thus, we believe that even an exact calculation would result in $(Ge_6)/(GaAs)_3$ (001) being metallic.

There is no *a priori* reason for the sign of the electric field in the (111) superlattice. Consider this superlattice to consist of bulk Ge to which we add a perturbation consisting of positive and negative charges on the As and Ga sites. If these charges were very small, linear-response theory would apply, and they would be partially screened by the electrons, leaving effective charges e^* of the original sign. If these charges were $+3e$, corresponding to CuBr, we can be fairly certain that the e^* would have the opposite sign to the bare perturbation, i.e., Cu would be the positive ion. GaAs lies between these two extremes and only by direct calculation can the sign of e^* be determined. An elementary calculation shows that if one assumes a lattice of point charges,[20]

$$E=2ze^*/a_0^3\epsilon_0 , \tag{2}$$

where $z=a_0/4\sqrt{3}$ is the smaller GaAs interplanar spacing. Taking the average of the field magnitudes in the center of the two quantum wells in Table I, we find

TABLE I. Electric fields as the midpoint between the two central atomic planes of each quantum well and the formation enthalpy per unit cell (or pair of interfaces) for ideal (110), (001), and (111) $(Ge)_6/(GaAs)_3$ superlattices and for five (111) superlattices with displacements as described in text.

	E_{GaAs} (V/Å)	E_{Ge} (V/Å)	H (meV)
(110)	0	0	389.5
(001)	−0.1009	+0.0992	637
(111)	+0.1146	−0.1112	235.6
(111)*A*	+0.1130	−0.1107	239.7
(111)*B*	+0.1120	−0.1112	250.3
(111)*C*	+0.1156	−0.1109	237.9
(111)*D*	+0.1077	−0.1058	232.0
(111)*F*	+0.1008	−0.1004	245.7

$e^*=0.069e$ with As positive.

We do not report valence-band offsets ΔE_v here although we[4] obtained exact agreement with experiment for $(GaAs)_3/(Ge)_6$ (110). The first step in calculating ΔE_v for $(GaAs)_n/(Ge)_{2n}$ is to obtain the difference between the average potentials in the Ge and GaAs central cells. In the (110) case, this potential difference changes only slightly as n goes from 3 to a large value. Because of the electric fields, this potential difference increases linearly with n, and ΔE_v is not even uniquely defined in the (001) and (111) superlattices.

Because of their large formation enthalpy, the (001) interfaces are likely to be unstable. This was previously concluded by BAH and PP because of the experimental[21] absence of interface acceptor states. The reconstructed interface could be either sharp or diffuse. Figure 3 shows a pair of sharp reconstructed (001) interfaces which are equivalent under a twofold rotation, so that there can be no electric field. Kunc and Martin[22] have carried out calculations for this interface in the virtual-crystal approximation. On the other hand, the ideal (111) interfaces may well be metastable against disproportionation and stable against reconstruction. We note that their formation enthalpy (including the contribution of the electric field) is only 60% of that of the nonpolar (110) interfaces. Thus, the speculation of Harrison *et al.*[13] that both (001) and (111) interfaces must reconstruct *in order to eliminate the electric field energy* is incorrect. Martin,[12] on the other hand, did not consider the electric field, *per se*. He calculated the energy of the reconstructed superlattice of Fig. 3 in a tight-binding approximation. Note that this unit cell contains 6 Ga, 6 As, and 12 Ge atoms. He compared this with the energy of an unreconstructed unit cell containing four As, three Ga, and five Ge atoms, and pointed out that this unit cell contains an extra electron which, because it must go into the conduction band, raises the total energy. Our unreconstructed unit cell contains equal numbers of Ga and As atoms and thus has no extra net charge although a bonding charge imbalance exists on each interface. Note that if one assumes ideal covalent bonding, each As contributes 1.25 electrons to each of four bonds in bulk GaAs and each Ga contributes 0.75. The interfacial As(Ga) atoms which have two bonds to Ge thus have a half an electron (hole) more than needed for bonding. Ideal covalency implies $e^*=1e$; thus, since $e^*=0.069e$, this contribution is reduced. However, as large as it is for (001) superlattices, it is approximately half as large for (111), where each interfacial As or Ga atom has only one Ge bond. Because the interfacial enthalpy is so much larger here than for GaAs/AlAs, we believe the bonding charge imbalance must be an important contribution. The (110) interface has both Ga—Ge and As—Ge bonds with their bonding charge imbalances of opposite sign. It had been believed that these would compensate, making (110) the lowest-energy interface. Since we find that it is not, we must conclude that the bonding-charge-imbalance contribution to the energy is a nearest-neighbor effect. This implies that reconstruction, when it does occur, occurs to reduce some other contribution to the total energy.

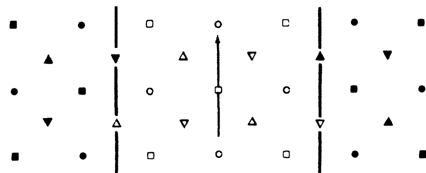

FIG. 3. Possible reconstructed interfaces for $(Ge)_6/(GaAs)_3$ (001). Vertical lines are interface planes. Arrow is twofold rotation axis. □ and ○ represent Ga (or As) atoms in the plane of the page $\frac{1}{2}a_0$ below. △ and ▽ represent As (or Ga) atoms $\frac{1}{4}a_0$ and $\frac{3}{4}a_0$ below the plane. ■, ▲, ●, and ▼ represent Ge atoms in the same positions.

Because a 0.03-eV indirect energy gap was obtained for the (111) superlattice, that calculation is fully self-consistent, and it is meaningful to ask what the effect of small displacements is on the electric field. In Fig. 2 the positive field will push the positive As and Ga ions to the right, and the negative field will push the Ge ions to the left. We thus considered rigid shifts of the GaAs quantum well relative to the Ge such that the Ge—As bond length increased and the Ga—Ge decreased. A, B, and C in Table I refer to shifts of $0.0025\sqrt{3}a_0$, $0.0050\sqrt{3}a_0$, and $-0.0025\sqrt{3}a_0$. We see that the positive shifts reduce E as expected, but they increase H. A parabolic fit yields an equilibrium shift of $-0.000\,36\sqrt{3}a_0$ and a negligible but positive increase in E. Rigid shifts of $\frac{1}{2}\delta$ of the Ga and As sublattices to the right and left, respectively, will increase z and give

$$\Delta E=\delta dE/dz=(2\delta/a_0^3\epsilon_0)(e^*+z\partial e^*/\partial z)$$
$$=(2\delta/a_0^3\epsilon_0)e^{**}\;. \quad (3)$$

D and F in Table I give E and H for $\delta=0.0025\sqrt{3}a_0$ and $0.0050\sqrt{3}a_0$. A parabolic fit yields an equilibrium $\delta=0.00\,176\sqrt{3}a_0$ which is equivalent to a 0.7% decrease in the length of the (111) bonds, and which results in about a 4% decrease in E. Had we allowed more general displacements (for example, had we allowed a strain of the unit cell in response to the inner displacements of the Ga and As sublattices, the equilibrium δ would have been larger), the net reduction of E might have gotten as large as 10%. Using the average Ge and GaAs ΔE from Table I in Eq. (3) gives $e^{**}=-0.126e$, of opposite sign to e^* and in agreement with the sign of the piezoelectric constant. This is in remarkably good agreement with the $-0.16e$ obtained by Martin and Kunc[23] who displaced planes of Ga atoms in opposite [001] directions rather than making a rigid displacement of the entire sublattice in the [111] direction.

Finally, we may ask what is to be expected for thicker (111) quantum wells. The electric field may be considered to be a consequence of the interfacial charge density resulting from the divergence of the bulk polarization arising from the $\pm e^*$ ionicity of the As and Ga atoms. Since the electric field has a bulk source, we do not expect the volume proportionality of the electric field energy to cause the interfaces to become unstable at some quantum-well thickness. For sufficiently thick quantum wells, electron and hole states will appear at the As and Ga interfaces and will screen the electric field. This

should further stabilize the interfaces. These interface states, which are forced out of the conduction and valence bands by the minima and maxima of the sawtooth potential, should not be confused with the intrinsic (001) interface states which are the *source* of the (001) electric fields.

In conclusion, we have made the first self-consistent calculations of electric fields in polar Ge/GaAs superlattices, found them to be extremely large, and in the (001) case, in the opposite direction to a previous prediction.[13] We also made the first *ab initio* calculation of the formation enthalpies of these interfaces and, contrary to all expectations, found the polar (111) interface appreciably lower than the nonpolar (110). Although one can never prove that there does not exist some other configuration of lower energy, we gave reasons for believing that the (111) interfaces are stable against reconstruction.

This work was supported by the Robert A. Welch Foundation (Houston, TX), the University of Texas Center for High Performance Computing, and by the National Science Foundation (NSF) under Grant No. DMR-87-18048.

---

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

[2]D. M. Bylander and L. Kleinman, Phys. Rev. B **38**, 7480 (1988).

[3]On the scale of 10^7 V/m the field was not constant over the central cell of each quantum well. Therefore, it is quite likely that the field would be even smaller in the central cell of a thicker quantum well.

[4]D. M. Bylander and L. Kleinman, Phys. Rev. B **39**, 5116 (1989).

[5]E. Louis, Solid State Commun. **24**, 849 (1977).

[6]B. Djafari-Rouhani, L. Dobrzynski, and M. Lannoo, Surf. Sci. **78**, 24 (1978).

[7]B. K. Agrawal, Phys. Rev. B **23**, 2995 (1981).

[8]M. Nishida, Surf. Sci. **109**, 557 (1981).

[9]G. A. Baraff, J. A. Appelbaum, and D. R. Hamann, Phys. Rev. Lett. **38**, 237 (1977); J. Vac. Sci. Technol. **14**, 999 (1977).

[10]J. Pollmann and S. Pantelides, Phys. Rev. B **21**, 709 (1980).

[11]This is the filling that would occur for a (100) GaAs slab terminated with Ga planes on *both* sides. Symmetry forbids an electric field in such a slab.

[12]R. M. Martin, J. Vac. Sci. Technol. **17**, 978 (1980).

[13]W. A. Harrison, E. A. Kraut, J. R. Waldrop, and R. W. Grant, Phys. Rev. B **18**, 4402 (1978).

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

[15]In the $\frac{1}{8}$ irreducible wedge of the $(\mathrm{Ge})_6/(\mathrm{GaAs})_3$ (001) BZ we sample the 12 points (in units of $2\pi/a_0$) $(\pm\frac{1}{8},\frac{1}{8},\frac{1}{12})$, $(\pm\frac{1}{8},\frac{3}{8},\frac{1}{12})$, $(\pm\frac{1}{8},\frac{5}{8},\frac{1}{12})$, $(\pm\frac{1}{8},\frac{7}{8},\frac{1}{12})$, $(\pm\frac{3}{8},\frac{3}{8},\frac{1}{12})$, and $(\pm\frac{3}{8},\frac{5}{8},\frac{1}{12})$.

[16]It is self-consistent within the approximation that the lowest 24 bands at each BZ point contribute to the charge density. If a more correct set of states is used, the change in the self-consistent potential will screen the *change* in the electric field. Thus, we do not expect our error to be large.

[17]Our calculated GaAs band gap is 0.540 eV without and 0.428 eV with spin-orbit interaction compared to the experimental 1.424 eV. Our calculated Ge band gaps are a direct band gap of 0.135 eV at the superlattice a_0 and an indirect one of 0.151 eV at the observed Ge a_0. Spin orbit will reduce these by about 0.1 eV. The experimental band gap is 0.74 eV (or 0.67 eV and 0 K). Thus, the GaAs band-gap correction is 1.00 eV and the Ge band-gap correction about 0.65 eV.

[18]Our sign convention is standard for E but not for V, which we take to be negative when attractive for electrons.

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

[20]e^* is a factor of 2 larger than one might naively calculate because E is arbitrary to within an additive constant which must be chosen to give periodic boundary conditions resulting in a Ge field whose average value is equal and opposite to the GaAs field.

[21]L. Esaki, W. E. Howard, and J. Heer, Surf. Sci. **2**, 127 (1964).

[22]K. Kunc and R. M. Martin, Phys. Rev. B **24**, 3445 (1981).

[23]R. M. Martin and K. Kunc, Phys. Rev. B **24**, 2081 (1981).