Stability and band offsets of heterovalent superlattices: Si/GaP, Ge/GaAs, and Si/GaAs

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First-principles pseudopotential theory is used to calculate the formation enthalpies ΔH and valence-band offsets for the heterovalent $(Si_2)_n/(GaP)_n$, $(Ge_2)_n/(GaAs)_n$, and $(Si_2)_n/(GaAs)_n$ superlattices with repeat periods $n \leq 4$ and growth directions $G\|[001]$, $[110]$, and $[111]$. All of these superlattices are found to be unstable with respect to phase separation; the $[111]$ system is the least unstable. The unreconstructed $[001]$ and $[111]$ polar superlattices have large internal electric fields, causing the $[001]$ superlattices to reconstruct for $n \geq 2$; $[111]$ are predicted to reconstruct for $n > 6$. Different types of reconstruction lead to different band offsets. A simple model for ΔH which includes the short-range nonoctet-bond energies and the long-range electrostatic interactions between donor and acceptor bonds is shown to capture the chemical trends of all calculated ΔH's.

Semiconductor superlattices (SL's) can be categorized as being either isovalent (e.g., Si/Ge, AlAs/GaAs, InAs/GaAs) or heterovalent (e.g., Ge/GaAs, Si/GaAs) and (nearly) lattice matched (e.g., AlAs/GaAs, Ge/GaAs) or lattice mismatched (e.g., Si/Ge, InAs/GaAs, Si/GaAs). Most previous studies of the thermodynamic stability of SL's (e.g., Refs. 1 and 2 and references therein) addressed isovalent SL's. There, the excess enthalpy ΔH per SL unit cell (energy with respect to equivalent amounts of the constituents at equilibrium) reflects an "interfacial energy" $2I$ due to both charge transfer near the interface and interfacial atomic relaxation, and the "constituent strain" (CS) energy $n \Delta E_{CS}$ due to the tensile and compressive strain of the n layers of the lattice-mismatched constituents. For lattice-matched SL's (Ref. 2) $\Delta E_{CS} = 0$ and ΔH equals a small[2] (~ 10 meV/cell) interfacial energy. In contrast, the interfacial energy of heterovalent SL's studied recently[3-7] differs from that in isovalent SL's in two ways: (i) The interface manifests nonoctet "wrong bonds"[7] of the IV-V and III-IV type which raise the energy relative to isovalent interfaces by about an order of magnitude.[4] In ideal $[001]$, $[111]$, and $[110]$ SL's the total number (N) of IV-V bonds equals the number of III-IV bonds; denoting by δ the average (relaxed) bond energy of the two bond types, the energy of a SL in orientation G contains a term $2N(G)\delta$. Since a $G\|[111]$ oriented SL has half as many nonoctet bonds ($N = 1$, per cell) as the $G\|[001]$ and $G\|[110]$ SL's (both $N = 2$), one would expect on this basis that the $[111]$ SL will be the most stable. (ii) Since a III-IV bond has a deficiency of $\frac{1}{4}$ electron and a IV-V bond has an excess of $\frac{1}{4}$ electron, these are expected to behave as acceptor and donor states, respectively, giving rise in uncompensated systems to partially occupied localized interface states.[3] Charge transfer (CT) from the IV-V donor bond to the III-IV acceptor bond leads to a lattice of charges and can lower ΔH by gaining the donor-acceptor energy difference (approximately the minimum band gap). The energy gain ΔE_{CT}, proportional to the magnitude $|q|$ of the compensation, depends also on the electrostatic energy of the ensuing arrangement of charged sites. Since in nonpolar $[110]$ SL's each interface

contains both donor and acceptor bonds, the CT occurs *within* a given interface and complete charge transfer ($q = \frac{1}{4}$) can be expected. On the other hand, in polar $[001]$ and $[111]$ SL's, each of the two interfaces contains a single type of nonoctet bond, and compensation thus involves *inter-interface* charge transfer, creating an oscillatory electric field[4] (running from the donor to the acceptor plane). This produces a potential drop across the SL, proportional to the charge transfer q and repeat period n. Since the potential drop cannot exceed the band gap, q must scale as $1/n$ for long periods n; complete compensation would then exist only for small n.

The above arguments suggest that for heterovalent SL's the enthalpy per cell can be written as

$$\Delta H = [2N(G)\delta + \Delta E_{CT}(q,n,G)] + n\Delta E_{CS}(G), \quad (1)$$

where the first two terms replace the interfacial energy $2I$ of isovalent SL's.[1,2] The dependence of ΔE_{CT} on q and on the configuration of compensation charges could then drive interfacial reconstructions[4-6] which minimize ΔH by balancing improved charge compensation against possible increase in the number N of nonoctet bonds. In particular, since the nonpolar $[110]$ SL is already fully compensated, it is expected to be stable against reconstruction. However, as previously discussed by several authors,[4-6] $[001]$ and $[111]$ SL's could reconstruct, e.g., by swapping half of the group-IV atoms (at the IV-V interface) with half of the group-III atoms (at the III-IV interface), thus creating a nonpolar interface with more effective, intra-interface compensation and with a more stable configuration of the compensation charges. This conserves N for $[001]$ SL's (thus, reconstruction could lower ΔH), but raises it for $[111]$ SL's (hence, need not).

Our first purpose in this work is to test these ideas quantitatively by calculating from first principles the left-hand side of Eq. (1) for three heterovalent SL's in a few repeat periods n, orientations G, and reconstruction models, and use these computed ΔH's to develop a simple analytic model [refinement of the right-hand side of Eq. (1)] which captures the essential physics and chemical trends in $\Delta H(n,G)$. We present a two parameter model that successfully describes all chemical trends in the calculated

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ΔH's; this model is then used to *predict* ΔH for geometries which are too complex to calculate directly. Our second purpose is to calculate the valence-band offsets ΔE_v of the superlattices lacking the oscillating electric fields; since ΔE_v depend strongly on the type of reconstruction, comparison to the measured ΔE_v could be used as a probe into the structure of the experimentally grown interfaces.[5,8]

We use the first-principles pseudopotential method[9,10] to calculate total energies and valence-band offsets as a function of the SL repeat period n (number of bilayers in each sublayer) and direction G. The lattice mismatched Si/GaAs SL's were coherently constrained to a Si substrate, whereas for the lattice-matched Si/GaP and Ge/GaAs SL's, the basal lattice constants (perpendicular to G) were chosen to be the average of the calculated equilibrium lattice constants of the constituents. Semi-relativistic pseudopotentials were generated using Kerker's method,[11] and the wave functions were expanded in plane waves with kinetic energies up to 15 Ry. The calculation is done self-consistently and the charge density is evaluated at the equivalent of two special k points[12] in an irreducible part of the fcc Brillouin zone. For some of the longer-period superlattices, no k-point set equivalent to the two fcc points exists[12] and larger equivalent sets were used (for both superlattices and constituents). Exchange and correlation are treated within the local-density approximation (LDA) using the electron-gas data of Ceperley and Alder as parametrized by Perdew and Zunger.[13] Atomic positions are determined by total-energy minimization.[9,10] This includes force relaxation for all cell-internal degrees of freedom as well as energy minimization with respect to c/a relaxation for all but the Si/GaP superlattices, where a c/a ratio of unity is assumed (based on our Ge/GaAs results, below). The valence-band offsets

are then computed for the equilibrium, minimum-energy configuration.

We calculate equilibrium lattice constants of 5.41, 5.41, 5.60, and 5.61 Å for pure Si, GaP, Ge, and GaAs, respectively. The experimental values[14] are 5.430, 5.450, 5.657, and 5.653 Å. For $n=2$ (001) SL's we consider four possible $c(2\times2)$ reconstructions: a III-IV (cation) swap or a IV-V (anion) swap; in each case we can swap atoms directly above one another in the [001] direction ("vertical") or atoms not directly above one another ("staggered").

Our calculated SL formation enthalpies are given in Table I. For the lattice-mismatched Si/GaAs system we also give the constituent-strain energy ΔE_{CS}, denoted as "$n=\infty$." Figure 1(a) depicts as solid circles the results for Si/GaP. Our ΔH values for Ge/GaAs are within 10 meV/cell of those calculated in Ref. 4 for G∥[001].

The results reveal the following trends: (i) All ΔH's are positive [and much larger than in isovalent SL's (Refs. 1 and 2)], hence these SL's are unstable thermodynamically towards phase separation, if equilibrium can be attained.

(ii) Because [111] SL's have only half as many nonoctet bonds as [001] and [110] SL's with the same n, the former have the lowest ΔH. Yet, Fig. 1(a) shows that despite the equal number of nonoctet bonds, $\Delta H([001])\neq\Delta H([110])$, and that these ΔH's have distinctly different n dependences. This reflects the fact that the [110] SL, having positive and negative charges in the *same* interface plane has lower electrostatic energy than the unreconstructed [001] SL where the positive and negative charges occur in *separated* interfacial planes. This sequence of stability [111] > [110] > [001] differs from that [111] > [001] > [110] of lattice-matched *isovalent* SL's (Ref. 2) lacking a field energy.

TABLE I. Calculated formation enthalpies (in units of eV/4-atom) of ideal and reconstructed heteropolar superlattices. The reconstructed superlattices are described in the text. The energies in parentheses refer to unrelaxed geometries with the atoms in their ideal zinc blende positions, others are relaxed energies. We estimate uncertainties of ≤ 0.02 eV.

| G	n	Reconstruction	Formation enthalpy Si-GaP	Ge-GaAs	Si-GaAs
[001]	1	no	0.49(0.50)	0.39(0.45)	0.49
		yes	(0.51)	(0.45)	⋯
	2	no	0.34(0.36)	0.26(0.27)	0.37
		cation vertical	0.22(0.25)	0.18(0.21)	0.25
		cation staggered	⋯	(0.23)	⋯
		anion vertical	0.24(0.25)	0.18(0.20)	0.27
		anion staggered	⋯	(0.23)	⋯
	3	no	0.23(0.26)	0.20(0.21)	⋯
	∞	no	0.0	0.0	0.04
[110]	1	no	0.49(0.50)	0.39(0.45)	0.51
	2	no	0.13(0.19)	0.12(0.15)	0.18
	3	no	0.11(0.15)	(0.14)	⋯
	4	no	0.07(0.10)	0.07(0.09)	0.13
	∞	no	0.0	0.0	0.05
[111]	1	no	0.12(0.17)	0.13(0.14)	0.19
	2	no	0.09(0.12)	⋯	0.16
	3	no	0.08(0.10)	⋯	⋯
	∞	no	0.0	0.0	0.05
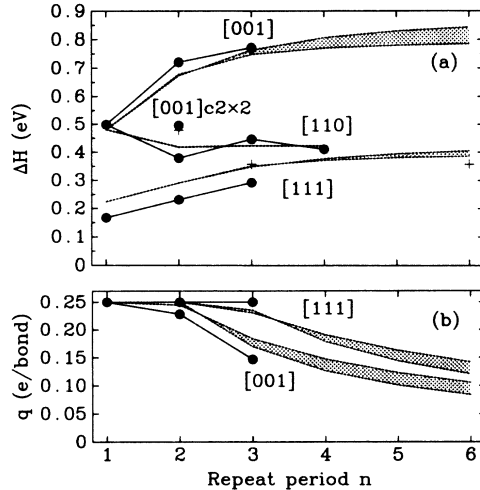
FIG. 1. Calculated (solid circles) and modeled [dashed lines and crosses, from Eq. (3)] formation enthalpies (a) per $4n$ atoms and (b) interinterface charge transfer (Ref. 15) of heterovalent (unrelaxed) Si/GaP superlattices. The zero of energy is taken as the energy of the separated constituents. The reconstructed superlattices are described in the text. The model energies correspond to a range of the parameters. The extreme values are $\Delta E_g(0) = 0.8$ eV, $\delta = 0.20$ eV, $U^D + U^A = 1.71$ eV, and $\Delta E_g(0) = 1.2$ eV, $\delta = 0.22$ eV, $U^D + U^A = 3.52$ eV.

(iii) As expected from above, our calculated electric fields run from the IV-V donor to the III-IV acceptor bond for all unreconstructed [001] and [111] SL's. This is in disagreement with the results of Bylander and co-workers[4] for Ge/GaAs, where the fields run in opposite directions in the [001] and [111] superlattices.

(iv) For the $n = 1$ [001] SL reconstruction is unstable (it raises the energy, see Table I), presumably because the layers are too thin. For $n = 2$ [001] all reconstructions lower ΔH considerably; the vertical swap is favored by a small amount. The energy difference between swapping the anion or cation is negligible for Ge/GaAs and favors a cation swap for Si/GaP and Si/GaAs. Since these energy differences are small, we cannot rule out a more complicated combination of anion and cation swaps as suggested in Ref. 5. For the [111] SL's complete intra-interfacial compensation can be achieved by swapping $\frac{1}{4}$ of the interface atoms. This, however, results in a 50% increase in the number of nonoctet bonds, and thus need not necessarily lower ΔH. We use our model ΔH below to study these [111] reconstructions.

(v) While it is commonly assumed[7] that the various nearest-neighbor bond lengths in systems whose constituents have the same cubic lattice constants (e.g., Si/GaP or Ge/GaAs) are equal to their "ideal" values, our total energy minimization shows that chemical interactions can drive bond-length changes. Compared with the ideal bond length $R^0 = (\sqrt{3}/4)a_{SL} = 2.339$ Å for Si/GaP (where a_{SL} is the SL lattice constant), we find that the Si–Ga bond lengths at the interface are longer by 2.3%, 1.9%, and 2.6%, and the Si–P bond lengths are shorter by 2.4%, 2.7%, and 3.3%, for [001], [110], and [111] SL's, respectively. For [111] SL's, the Ga–P bonds at the center of

the GaP layer are split into short ($\delta R = -1.4\%$, parallel to [111]) and long ($\delta R = +0.3\%$, perpendicular to [111]) bonds, reflecting piezoelectric effects.

(vi) We calculated valence-band offsets using the superlattices to obtain potential offsets.[16] For interfaces with residual electric fields, an offset calculation is impossible. Our results for the nonpolar [110] and the reconstructed [001] interfaces (obtained from relaxed $n = 4$ and unrelaxed $n = 2$ SL's, respectively) are given in Table II. For the lattice-mismatched Si/GaAs system on Si, we give the offset for the average of the strain split valence-band maximum of GaAs. For the [110] Ge/GaAs interface, our $\Delta E_v = 0.48$ eV is in good agreement both with experiment,[8] 0.56 eV, and with most previous calculations: 0.51,[17] 0.54,[18] 0.56,[4] and 0.63 eV (Ref. 19) (although Tersoff[20] finds 0.32 eV). For the reconstructed [001] Ge/GaAs our results agree with those of Kunc and Martin[21] and of Baroni, Resta, and Baldereschi[18] to within 0.1 eV, even though they ignored relaxations and used "averaged virtual atoms" rather than real Ge, Ga, and As atoms at the interfaces. (Their calculated total energies[21] clearly suffered from this choice.) Note that the anion and cation [001] reconstructed interfaces give rise to very different band offsets even though their formation enthalpies are virtually the same, and that the average of the two offsets is close to the [110] offset. This is in accord with the results of Harrison et al.[5] Our calculated $\Delta E_v = 0.45$ eV for [110] Si/GaP can be compared with the results of other self-consistent calculations: 0.45,[20] 0.53,[17] 0.61,[19] and 0.77 eV.[22] An experimental value of 0.80 eV (Ref. 23) is frequently quoted,[17,19,22] but Niles and Hochst[24] have recently suggested that their photoemission experiments may well imply a different offset.

We now use our directly calculated ΔH's of Table I to develop a simple physical model. To model ΔE_{CT} we apply linear response theory to the LDA total-energy expression,[9] and assume that the donor and acceptor states have a nonoverlapping, spherical charge distribution centered at the bonds. Assuming that the band widths of these interface states are independent of G, the difference between the donor and acceptor energy levels, to first order in q, is

$$E_g(q) = E_g(0) - (\epsilon_0)^{-1}(V^D_{\text{Madelung}} + V^A_{\text{Madelung}})q$$
$$- (U^D + U^A)q, \qquad (2)$$

where $E_g(0)$ is the uncompensated donor-acceptor energy difference, V^D_{Madelung} and V^A_{Madelung} are the electrostatic Madelung potentials at the donor and acceptor bonds, respectively, resulting from an unscreened charge transfer

TABLE II. Calculated valence-band offsets (in eV) for (001) reconstructed and (110) unreconstructed superlattices. A positive valence-band offset puts the valence-band maximum on the column IV sublattice.

G	Reconstruction	Valence-band offset		
		Si-GaP	Ge-GaAs	Si-GaAs
[001]	cation vertical	0.8	0.7	0.3
	anion vertical	0.0	0.1	−0.5
[110]	none	0.45	0.48	−0.06

of one electron, ϵ_0 is the static dielectric constant, and U^D and U^A are the intrabond electron repulsion (including both electrostatic and exchange-correlation contributions). Using Janak's theorem,[25] the integral

$$\Delta E_{CT} = -\int_0^q E_g \, dq$$

is the total energy change upon a donor-to-acceptor charge transfer q. Thus, ΔH (per $4n$ atoms) becomes $2I + n \Delta E_{CS}$, where

$$2I/N = 2\delta - E_g(0)q + (2\epsilon_0)^{-1}[V^D_{Madelung}(n,G) + V^A_{Madelung}(n,G)]q^2 + \tfrac{1}{2}(U^D + U^A)q^2 , \qquad (3)$$

where $N = 1$ for [111] and $N = 2$ for [001] and [110]. The charge transfer q is calculated from Eq. (2) by setting $E_g(q) = 0$ and then limiting q to a maximum of $\tfrac{1}{4}$ electrons. If the resulting q is less than $\tfrac{1}{4}$ [i.e., long n's; see Fig. 1(b)] Eq. (3) can be written as

$$2I/N = 2\delta - \tfrac{1}{2}E_g(0)q , \qquad (4)$$

i.e., the energy gain is proportional to $1/n$. For the short-period superlattices studied here, q achieves close to its fully compensated value ($\tfrac{1}{4}$) in all cases except for $n = 3$ [001] [Fig. 1(b)]. This prevents us from fitting independently all parameters of Eq. (3). To improve the robustness of the fit, we also fit the $n = 3$ charge transfer (calculated[15] to be 0.15 electrons) in addition to the total energies. The Madelung energy is calculated by the Ewald method and ϵ_0 is set to the average (10.4) of Si and GaP. Our fitting parameters are δ and $(U^D + U^A)$. As seen in Fig. 1, the results are insensitive to $E_g(0)$ over a range of values [since changes in $E_g(0)$ are offset by changes in $U^D + U^A$]. The accuracy of the model is remarkable considering its simplicity. In particular, we have assumed that charges on neighboring bonds (which occur in the [001] and the reconstructed [111] SL's) are taken to be fully screened (using ϵ_0). This assumption can be relaxed and the fit can be improved by a factor of 2 by introducing one additional parameter to account for the repulsion between equal charges on neighboring bonds.

Had one neglected[7] the compensation energy, one would have, by Eq. (3) $\Delta H([001],n) = \delta H([110],n) = 4\delta$

$= 0.8$ eV/cell and $\Delta H([111],n) = 2\delta = 0.4$ eV/cell for all n's, which is clearly not the case [Fig. 1(a)]: The compensation energy lowers ΔH in all cases, and introduces distinct n and G dependences. For long periods, the unreconstructed $\Delta H([001])$ and $\Delta H([111])$ approach their uncompensated values 4δ and 2δ asymptotically like $1/n$. For short periods all superlattices are nearly completely compensated ($q \simeq \tfrac{1}{4}$), and the difference between $\Delta H([001],n = 2)$ and $\Delta H([110],n = 2)$ lies in the more favorable Madelung energy of the nonpolar [110] interfaces. The $c(2\times2)$ reconstruction of the [001] interfaces thus nearly recovers all of this extra electrostatic stabilization energy.

Using our model we can investigate other possible structures for which direct calculations are difficult. Figure 1(a) shows (dashed lines) the model energies of some longer period superlattices. In the figure we show the results for a range of $\Delta E_g(0)$ between 0.8 and 1.2 eV, resulting in a modest spread (shaded regions) in the predictions. We also show (crosses) the estimated energies for the reconstructed [111] superlattices with a vertical cation or anion swap (the model does not distinguish between the two). The model predicts that the $n = 3$ superlattice is marginally stable against reconstruction, but that the $n = 6$ SL is not.

The success of this model in reproducing the trends of the first-principles results suggests that it can be used to describe nonisovalent alloys, treated previously[7] without electrostatic terms.

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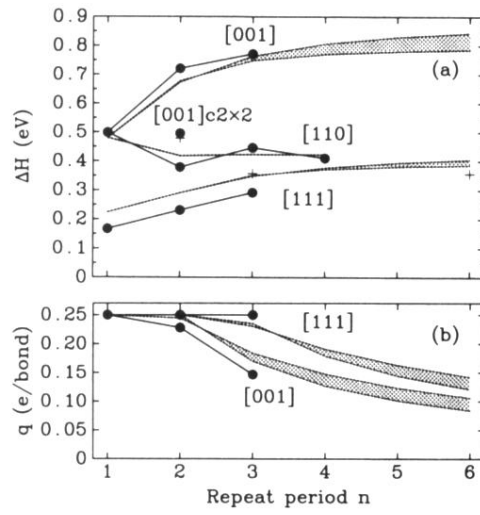[25]J. F. Janak, Phys. Rev. B 18, 7165 (1978).

FIG. 1. Calculated (solid circles) and modeled [dashed lines and crosses, from Eq. (3)] formation enthalpies (a) per $4n$ atoms and (b) interinterface charge transfer (Ref. 15) of heterovalent (unrelaxed) Si/GaP superlattices. The zero of energy is taken as the energy of the separated constituents. The reconstructed superlattices are described in the text. The model energies correspond to a range of the parameters. The extreme values are $\Delta E_g(0) = 0.8$ eV, $\delta = 0.20$ eV, $U^D + U^A = 1.71$ eV, and $\Delta E_g(0) = 1.2$ eV, $\delta = 0.22$ eV, $U^D + U^A = 3.52$ eV.