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Theory of interfacial stability of semiconductor superlattices

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With few exceptions, abrupt isovalent AC/BC semiconductor superlattices (SL's) were predicted previously to be *globally* unstable at $T = 0$ with respect to the random alloy. We examine the stability of these SL's with respect to *local* swaps of atoms near the interface, leading to interface-broadening reconstructions. For lattice-mismatched GaP/InP SL's, we find that reconstruction is most energetically favorable for SL's in the [111] and [011] directions, and somewhat less favorable for SL's in the [001] direction. These results are independent of period p for $p > 3$; for $p < 3$, reconstruction results in large energy gains (nearly 60% for $p = 1$ [111]) in the [001] and [111] directions, but reconstruction is unfavorable for short-period [011] and [201] SL's. For monolayer SL's, reconstruction is accompanied by a large increase in the electronic band gap. The stability of abrupt SL's with respect to reconstruction shows a strong dependence on the substrate lattice constant on which the SL is grown; SL's grown in a GaP substrate are the most stable, while those grown on InP are the least stable. For *lattice-matched* AlAs/GaAs SL's, small energy lowerings are found for some SL's with $p \leq 3$, while no reconstructions are found for longer periods.

I. INTRODUCTION

The interface abruptness of a semiconductor superlattice (SL) is the most important measure of its quality. Thermodynamics can provide two obstacles to perfectly abrupt interfaces. First, at high temperatures, disordering of the SL is favored by the entropy term $-TS$. Second, even at $T = 0$, an abrupt, ordered superlattice could have a higher formation enthalpy than the random alloy. Indeed, a real interface is typically a region of several atomic layers whose composition changes gradually from that of pure AC to that of pure BC ("graded interface"). The most abrupt SL's grown to date still have graded interfaces with thickness of about two layers of the crystal.[1] The quality of the interface region can change the electronic properties of the SL. For example, the electron-confinement energy in AlAs/GaAs SL's is predicted to increase as the interface becomes more graded.[2] The relationship between interface reconstruction and the band offset was studied by Hybertsen,[3,4] and by Dandrea and co-workers.[5,6]

At finite temperatures, entropy always enhances both local atomic interchanges and, eventually, global mixing (randomization). The question that we address here is whether the internal (configurational) energy encourages or discourages mixing. Consider, for example, short-period SL's. There are materials that naturally crystallize as short-period SL's, such as the $(AC)_1(BC)_1$ [001] SL—the metallic CuAu-I compound ($L1_0$)—or the $(AC)_2(BC)_2$ [201] SL—the chalcopyrite compound. For such materials, the ordered abrupt SL structure is the $T = 0$ ground state in that they are thermodynamically stable with respect to both local atomic rearrangements and global structural transformations. However, for *isovalent* short-period SL's, first-principles calculations show that almost all III-V and II-VI SL's with abrupt interfaces have higher $T = 0$ energy than their phase-separated constituents,[7-12] and in many cases, higher than the random alloy.[7] This means that most abrupt SL's are unstable *globally*. Large activation barriers for atomic rearrangement may, however, prevent these instabilities from being seen in the laboratory.

In this paper, we consider instead the *local* stability of SL's with respect to atomic swaps about the interface, resulting in interfaces that are graded over two layers of the crystal. We compare the formation enthalpies perfect (abrupt) interface with those obtained from the perfect interface by swapping up to two-thirds of the A and B atoms from the layers on either side of the interface. Using a variety of theoretical techniques, we investigate over 150 different swap geometries for AlAs/GaAs and GaP/InP SL's in the [001], [011], [111], and [201] directions.

We identify the most energy-lowering reconstructions as a function of the superlattice period and orientation. For lattice-mismatched GaP/InP SL's, we find that there is always some reconstruction pattern that has a lower $T = 0$ energy than the abrupt SL, except for the short-period [011] and [201] SL's. Energy lowerings in GaP/InP SL's due to interface reconstruction can be very large—for the CuPt-like structure (a $(\mathrm{GaP})_1/(\mathrm{InP})_1$ SL in the [111] direction) reconstruction reduces the formation energy nearly 60%. This result contrasts sharply with the behavior of the CuPt-like structure at one or a few layers below a free (001) surface, where Ga↔In swaps are predicted[13,14] to *increase* the total energy. This highlights the difference between surface reconstruction and interface reconstruction. Changing the substrate lattice constant on which the SL is grown has a significant effect on the energetics of reconstruction: reconstruction is enhanced for GaP/InP SL's grown on an InP substrate, but is suppressed when grown on a GaP substrate. For monolayer GaP/InP SL's, we show that the reconstruction produces large increases in the band gap. For lattice-matched AlAs/GaAs we find that reconstructions are energy lowering only for SL's of periods 1 and 2. Longer period SL's are found to be stable with respect to reconstruction. Our results can be analyzed in terms of reconstruction-induced changes in the symmetries of the bonds near the interface.

II. DESCRIBING RECONSTRUCTIONS

In this section we describe the identification of the SL reconstructions. Most of the reconstructions considered here are formed by swapping atoms between the two layers that adjoin the interface on either side. (The total number of atoms of each type is preserved by the reconstruction.) Towards the end of this paper we will consider briefly the changes in total energy when the intermixed layers are separated from one another. We will deal only with superlattices formed from two zinc-blende constituents with a common ion (as in AlAs/GaAs). Hence, the reconstructions that we examine will be those formed by swapping the noncommon ions (Al↔Ga swaps). We will not examine swaps between cations and anions, as these contain high-energy antisite defects.[15]

The identities of the swaps are independent of the superlattice period p. That is, the same pattern of atomic rearrangement can exist in SL's of $p = 1, 2, 3, \ldots$, but the properties of the reconstructed superlattices will depend on p. The total number of possible reconstructions of an SL will, however, depend on p. This is because two reconstructions that are distinct for one period may be be identical for a different period. As a rule, there are far fewer distinct reconstructions for $p = 1$ and $p = 2$ SL's than for longer-period SL's. (The same thing happens with abrupt SL's in different directions: SL's in the [001] and [011] directions are distinct for $p > 1$, but identical for $p = 1$.)

The reconstructions are taken to repeat in the interface plane; the periodicity of the reconstruction in the interface plane (not to be confused with the superlattice period p in the direction perpendicular to the layer planes) defines an interface unit cell. The interface unit cell is analogous to the surface unit cell of a reconstructed surface. We will use the same notation as that used for surface reconstructions: "2×2" denotes an interface cell with real-space lattice vectors $2\mathbf{a}_1, 2\mathbf{a}_2$, where $\mathbf{a}_1, \mathbf{a}_2$ are lattice vectors in the interface plane of the ideal SL. Although the term reconstruction is generally used for structural rearrangements, we apply the term to chemical changes, in which the lattice sites remain unchanged (although these chemical changes will, in general, cause additional atomic relaxations). For [001] SL's we adopt the convention that $\mathbf{a}_1 \parallel [110]$ and $\mathbf{a}_2 \parallel [\bar{1}10]$, where a cation is located at $\mathbf{0}$. For [011] SL's, $\mathbf{a}_1 \parallel [0\bar{1}1]$ and $\mathbf{a}_2 \parallel [100]$. For [201] SL's, $\mathbf{a}_1 \parallel [010]$ and $\mathbf{a}_2 \parallel [\bar{1}\bar{1}2]$.

Our calculations are done for superlattices in which the interface going from Al to Ga (for AlAs/GaAs), or from Ga to In (for GaP/InP), is reconstructed, while the reverse interface is abrupt. We examine interface reconstructions with two-dimensional unit cells of up to four atoms each. The unit cells are 2×1, 1×2, $\sqrt{2}\times\sqrt{2}$, 3×1, 1×3, 4×1, 1×4, 2×2 for the [001] and [011] directions, 2×1, 3×1, $\sqrt{3}\times\sqrt{3}$, 4×1, 2×2 for the [111] direction, and 2×1, 1×2, 3×1, 1×3, $\sqrt{3}\times\sqrt{3}$, 4×1, 1×4, 2×2 for the [201] direction. Figures 1–4 show several of the unit cells for each of these SL directions.

We consider all reconstructions that swap up to two-thirds of the atoms in the unit cell. The atoms in each unit cell are labeled $L1$, $L2$, ..., for atoms in the plane beneath the interface and $U1$, $U2$, ..., for atoms in the plane above the interface (Figs. 1–4). Thus each reconstruction is uniquely identified by its interface unit cell and a list of the atoms in the layer below and above the

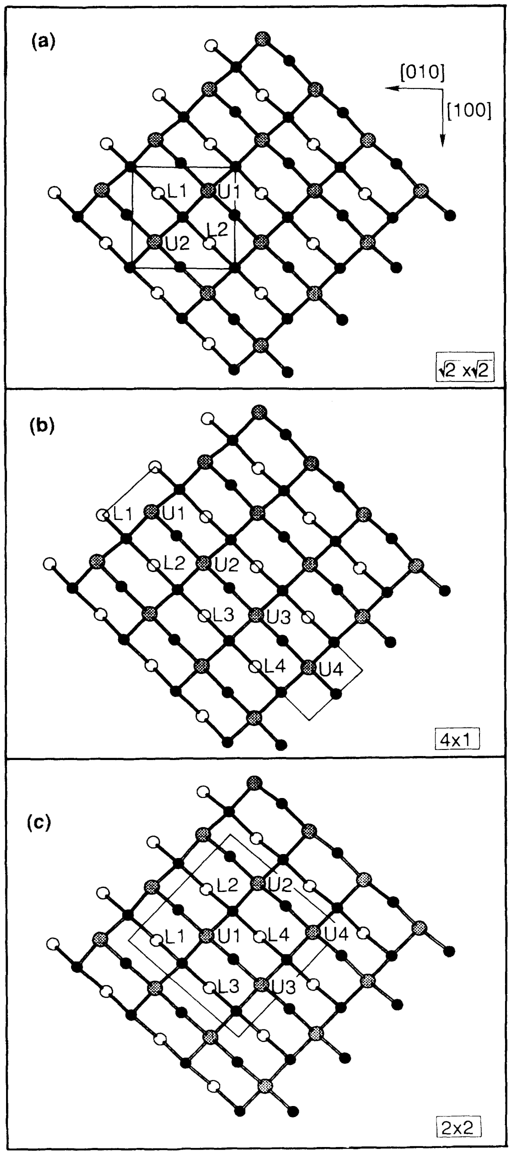

FIG. 1. Some of the unit cells for reconstructions of [001] SL's. For AlAs/GaAs SL's, the white, shaded and solid atoms represent Al, Ga and As, respectively. For GaP/InP, the corresponding identifications are Ga, In, and P.

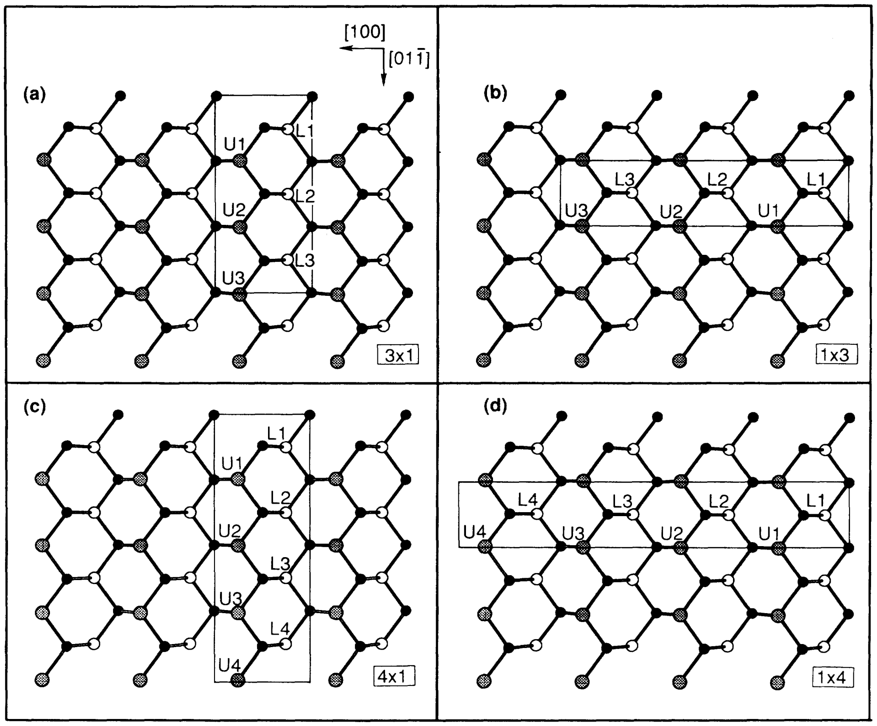

FIG. 2. Some of the unit cells for reconstructions of [011] SL's. Identifications of atoms are the same as in Fig. 1.

interface (equal numbers of atoms on each side) that are swapped. Not all possible swaps are distinct: for example, in the 2×1 unit cell for an [001] SL, the reconstruction obtained by swapping the pairs ($L2$, $U2$) is identical with that obtained by swapping ($L1$, $U1$). Thus any list of swaps must be checked to eliminate double counting. All of the abrupt and reconstructed SL's that we consider here contain equal amounts of AC and BC.

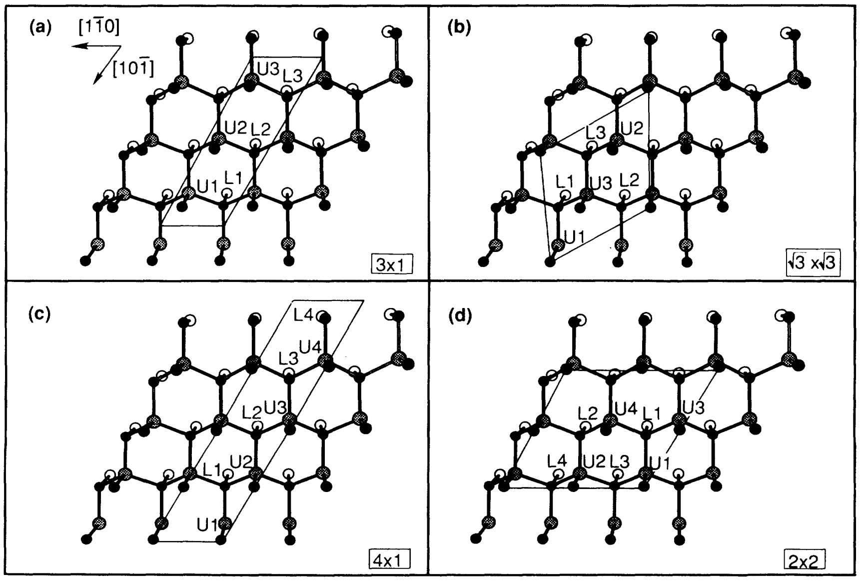

FIG. 3. Some of the unit cells for reconstructions of [111] SL's. Identifications of atoms are the same as in Fig. 1.

III. CALCULATING RECONSTRUCTION ENERGIES

We now describe the methods used to calculate the formation enthalpies of both the abrupt and reconstructed SL's. The $T = 0$ formation enthalpy, per four-atom unit, of an $(AC)_p(BC)_p$ SL is

$$\Delta H[(AC)_p(BC)_p] = \frac{E[(AC)_p(BC)_p]}{p} - E[AC] - E[BC], \tag{1}$$

where $E[(AC)_p(BC)_p]$ is the total energy of the SL, and $E[AC]$ and $E[BC]$ are the energies of the constituents at equilibrium. Section II shows that a survey of the important interfacial reconstructions involves very many (more than 150) different structures, with up to 96 atoms per unit cell. We use three different techniques to calculate the formation enthalpies of the abrupt and reconstructed SL's: cluster expansion, valence-force field model, and first-principles density-functional calculations with nonlocal pseudopotentials.

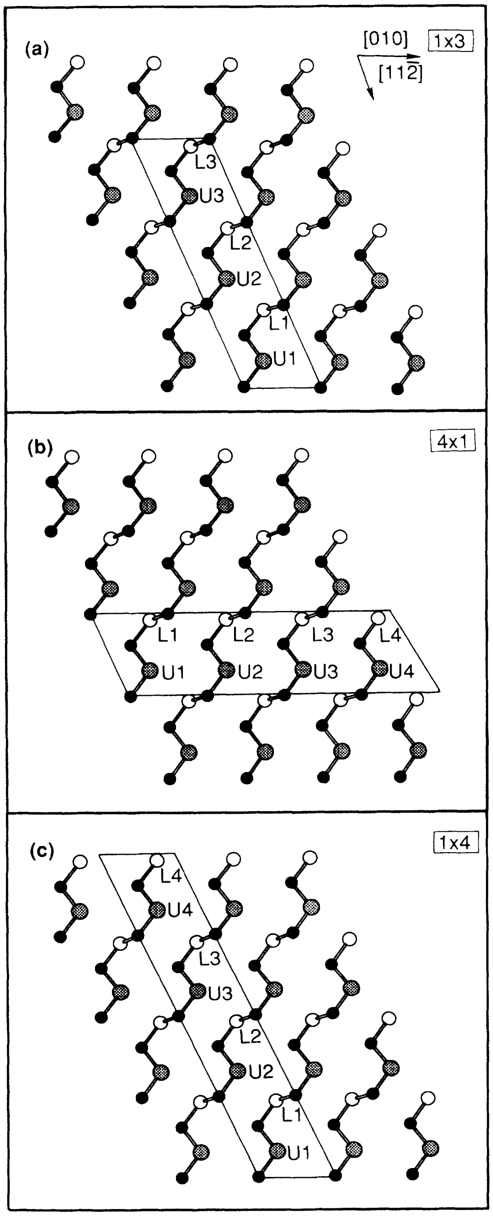

FIG. 4. Some of the unit cells for reconstructions of [201] SL's. Identifications of atoms are the same as in Fig. 1.

In lattice-matched systems, such as AlAs/GaAs, the strain energy vanishes and the entire formation enthalpy is given by the chemical energy associated with charge redistribution.[16] These energies can be calculated with self-consistent total-energy methods, or with a cluster expansion[16–19] constructed from the total-energy calculations. We will describe the formation enthalpies of the AlAs/GaAs system with a cluster expansion, based on first-principles electronic structure calculations.[18] In the cluster expansion method an AC/BC structure is treated as a lattice gas in which each site of a fcc lattice can be occupied by either A atoms or B atoms. (The C sublattice is always fully occupied by C atoms.) The lattices sites occupied by A atoms are assigned spin -1, while those occupied by B atoms are assigned spin $+1$. The energies of the different structures are mapped onto a generalized Ising Hamiltonian. The values of the non-negligible interaction energies (such as pair, three-body, and four-body interactions) are determined from a fit to the results of first-principles total-energy calculations for a small set of structures. These interaction energies are then used to predict the energies of new structures, using just their spin variables. Magri, Bernard, and Zunger[19] have applied this procedure to AlAs/GaAs structures and found that the cluster expansion predicts the results of *ab initio* total-energy calculations with an accuracy of better than 0.1 meV per atom. We use this cluster expansion, with interaction energies taken from Ref. 19, to predict the formation enthalpies of the reconstructed AlAs/GaAs structures. With the cluster expansion we can calculate quickly the formation energy of a large number of SL reconstructions with the accuracy of full electronic structure calculations.

In size-mismatched systems, such as GaP/InP, the contribution to the formation enthalpy from elastic energies[7] (due both to biaxial deformations and to local strain-relieving atomic relaxations) is much larger than that from chemical energies. We use use a Keating valence-force field (VFF) model (with the parameters from Ref. 20) to describe the strain energies. Because all of the reconstructions considered here preserve the fourfold coordination, and contain neither broken bond nor antisite defects, the VFF model suffices. Indeed, in previous work,[7] it was found that the VFF model correctly predicts the trends of the total-energy calculations, even in the presence of massive bond bending and stretching. To examine the accuracy of the VFF predictions, we use first-principles total-energy calculations to calculate the formation enthalpies of the reconstructions that were found to have the lowest strain energy in the VFF model.

The first-principles total-energy calculations[21] were performed using density-functional theory in the local-density approximation (LDA) and norm-conserving nonlocal pseudopotentials.[22] Atomic relaxations were first determined from the VFF model (here the theoretically determined equilibrium bond lengths were used, rather than the experimental bond lengths), and subsequently refined by Hellman-Feynman force calculations in the pseudopotential total-energy calculations. In every case, the atomic relaxations predicted by the VFF model were converged to better than 1 meV per atom in the pseudopotential total-energy calculations. The energy cutoff used in the calculations was 15 Ry, and in each case, equivalent sets of special k points[23] were used for bulk GaP and InP (whose energies are needed to derive ΔH), the abrupt SL's, and the reconstructed SL's. The uncertainty due to the k-point sampling is estimated to be about 5 meV per four-atom unit. The Ceperley-Alder[24,25] correlation was used. Comparison of these first-principles results—including both chemical and elastic effects—with pure VFF calculations—including only elastic effects—confirms that elastic effects are dominant.

IV. RESULTS

A. Lattice-matched AlAs/GaAs superlattices

Our results for AlAs/GaAs reconstructions are shown in Table I. The individual reconstructions are identified in Table II. Because the system is lattice matched (so that there is no strain energy), the energy gains due to reconstruction are small. Figure 5(a) shows the calculated energy lowerings for some of the $p = 1$ and $p = 2$ structures.

The AlAs/GaAs results follow a simple trend. AlAs/GaAs structures prefer to phase separate at $T = 0$. Thus the lowest-energy structures have the most next nearest neighbors of the same type, so that the system prefers to maximize the number of like-atom pairs. This explains why energy-lowering relaxations are found only for $p \leq 2$ SL's (Table I), where the layers are so thin that some reconstructions can actually decrease the mixing of the constituents, compared to the abrupt SL. For longer period SL's, any reconstruction increases the number of Al-Ga pairs, which is energetically unfavorable. All abrupt AlAs/GaAs SL's are energetically stable for $p > 3$, only the [111] and [001] are stable for $p = 2$, while none are stable for $p = 1$. At growth temperatures, however, entropic terms will give rise to disorder, since the random alloy is the ground state at these temperatures.[18] We have confirmed the accuracy of the cluster expansion predictions by explicit pseudopotential calculations for four different reconstructions. The largest prediction error that we found was 0.3 meV per four-atom unit, so that the error bar of the cluster expansion prediction is less than the intrinsic error bar of the underlying pseudopotential calculations.

These results complement the recent work of Heinemann and Scheffler[15] on point defects in AlAs/GaAs (100) interfaces. They studied *isolated* point defects at the interface—as opposed to the *periodic* reconstructions studied here—and found that the $\mathrm{Al}_{\mathrm{Ga}}$ and $\mathrm{Ga}_{\mathrm{Al}}$ defects have a very low formation energy. Both their results and our own show that for long-period SL's there is no energy gain from swapping Al and Ga atoms across the interface. Since the $T = 0$ energetics do not drive the broadening of SL's with $p > 3$, we conclude that either entropic forces or the details of the growth process are the factors that prevent the formation of perfectly abrupt AlAs/GaAs interfaces.

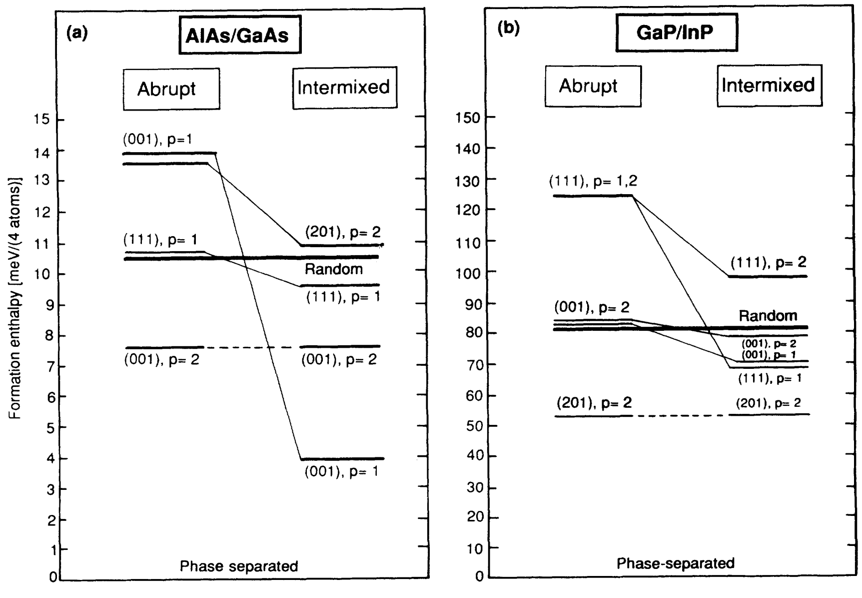

FIG. 5. Energy lowerings due to reconstruction in AlAs/GaAs (from cluster expansion) and GaP/InP (from VFF) SL's for $p = 1, 2$. Reconstruction patterns are identified in Table II for AlAs/GaAs and in Table IV for GaP/InP.

TABLE I. Formation energies ΔH (in meV per four-atom unit) for $(\mathrm{AlAs})_p/(\mathrm{GaAs})_p$ SL's with orientation **G**, from the cluster expansion. The reconstructed energy is for the lowest-energy reconstruction found. A blank entry for reconstructed means that all reconstructions raised the SL energy. The individual reconstructions are identified in Table II. For comparison, the predicted formation energy of the random $x = \frac{1}{2}$ alloy is 10.6 meV per four-atom unit.

	ΔH (meV per four-atom unit) for period p					
G	$p=1$	$p=2$	$p=3$	$p=4$	$p=5$	$p=6$
[001]						
Abrupt	13.7	7.6	5.0	3.8	3.0	2.5
Reconstructed	3.8					
[011]						
Abrupt	13.7	10.6	7.3	5.5	4.4	3.7
Reconstructed	3.8	9.5				
[111]						
Abrupt	10.7	5.7	3.8	2.9	2.3	1.9
Reconstructed	9.6					
[201]						
Abrupt	13.7	13.5	11.7	9.1	7.3	6.1
Reconstructed	3.8	10.8	10.7			

The cluster expansion predicts 10.6 meV per four-atom unit for the energy of the random $\mathrm{Al_{0.5}Ga_{0.5}As}$ alloy. Comparing with the results of Table I, we see that the reconstructed SL's are more stable than the random alloy for [011] $p = 1, 2$, and [111] $p = 1$, while the corresponding abrupt SL's are less stable than the random alloy.

B. Lattice-mismatched GaP/InP superlattices

Table III shows the VFF predictions for the most energy-lowering reconstructions in GaP/InP SL's, where the SL is free-floating (i.e., the formation enthalpy ΔH is minimized with respect to the unconstrained SL lattice constant). The identification of the most energy-lowering swaps for GaP/InP SL's, when grown on the equilibrium lattice constant, is given in Table IV. Figure 5(b) shows the calculated energy lowerings for some of the $p = 1$ and $p = 2$ structures. Energy-lowering reconstructions are found in all cases except [011] $p = 2$, and [201] $p = 2, 3$. Table V gives first-principles results for some of the stablest reconstructions. The pseudopotential results for the abrupt SL's agree to within 10% with the all-electron results of Dandrea *et al.*[7] In all cases, the first-principles results and the VFF results exhibit the same trends, but the VFF model underestimates the energy lowerings due to reconstruction. This means that the small chemical energy, which is not included in VFF, is also lowered by the reconstruction. The behavior of GaP/InP SL's is quite different from that of AlAs/GaAs SL's. Here reconstruction can lead to large energy gains, especially for the shorter period superlattices. The most significant example of this is for the [111] $p = 1$ SL (CuPt structure), where ΔH of the abrupt SL is 156 meV per four-atom unit, while that of the lowest-energy reconstruction, with $\frac{1}{3}$ of the cations swapped ($\sqrt{3} \times \sqrt{3}$ with atoms $L1$ and $U1$ swapped), is 68 meV per four-atom unit. This re-

TABLE II. Identification of the most energy-lowering swaps for AlAs/GaAs SL's. For each swap, we present the fraction of cations in the interface planes that are swapped, the interface unit cell, which atoms in the unit cell are swapped (where the identifications are referred to the appropriate figure), and the lowering of the interfacial energy due to the reconstruction $(J - I)$ in meV/(interface unit). For $p = 1$, the [001], [011], and [201] SL's are identical; the lowest-energy reconstruction is found when the atoms are swapped across the [011] plane.

Superlattice	Fraction swapped	Unit cell	Atoms swapped	Figure	$J-I$
$p=1$ [001]		See $p=1$ [011]			
$p=1$ [011]	$\frac{1}{2}$	1×4	$(L1, L2) \leftrightarrow (U1, U3)$	2(d)	−9.9
$p=2$ [011]	$\frac{1}{3}$	1×3	$L1 \leftrightarrow U2$	2(b)	−2.2
$p=1$ [111]	$\frac{1}{3}$	3×1	$L1 \leftrightarrow U3$	3(a)	−1.2
$p=1$ [201]		See $p=1$ [011]			
$p=2$ [201]	$\frac{1}{2}$	4×1	$(L1, L2) \leftrightarrow (U3, U4)$	4(b)	−5.6
$p=3$ [201]	$\frac{1}{2}$	1×4	$(L1, L2) \leftrightarrow (U1, U4)$	4(c)	−2.7

TABLE III. VFF predictions for the lowest-energy reconstructions of GaP/InP SL's. Formation energies ΔH, in meV per four-atom unit for SL grown on the minimum-energy substrate lattice constant (typically 5.61–5.62 Å). The individual reconstructions are identified in Table IV. A blank entry for reconstructed means that all reconstructions raised the SL energy. For comparison, the VFF prediction for the formation energy of the random $x = \frac{1}{2}$ alloy is 82 meV per four-atom unit.

	ΔH (meV per four-atom unit) for period p					
G	$p = 1$	$p = 2$	$p = 3$	$p = 4$	$p = 5$	$p = 6$
[001]						
Abrupt	81	84	85	86	86	87
Reconstructed	70	78	81	83	84	85
[011]						
Abrupt	81	72	92	97	101	103
Reconstructed	70		78	91	94	98
[111]						
Abrupt	124	123	122	122	122	122
Reconstructed	68	97	106	110	112	114
[201]						
Abrupt	81	53	70	79	86	87
Reconstructed	70			77	82	87

TABLE IV. Identification of the most energy-lowering swaps for GaP/InP SL's, when grown on the equilibrium lattice constant. For each swap, we present the fraction of cations in the interface planes that are swapped, the interface unit cell, which atoms in the unit cell are swapped (where the identifications are referred to the appropriate figure), and the lowering of the interfacial energy due to the reconstruction $(J - I)$ in meV/(interface unit). For $p = 1$, the [001], [011], and [201] SL's are identical; the lowest-energy reconstruction is found when the atoms are swapped across the [001] plane.

Superlattice	Fraction swapped	Unit cell	Atoms swapped	Figure	$J - I$
$p = 1$ [001]	$\frac{1}{2}$	4×1	$(L1, L2) \leftrightarrow (U1, U2)$	1(b)	−11
$p \geq 2$ [001]	$\frac{1}{2}$	$\sqrt{2} \times \sqrt{2}$	$L1 \leftrightarrow U1$	1(a)	−11
$p = 1$ [011]		See $p = 1$ [001]			
$p \geq 3$ [011]	$\frac{2}{3}$	3×1	$(L1, L2) \leftrightarrow (U1, U2)$	2(a)	−27
$p \geq 1$ [111]	$\frac{1}{3}$	$\sqrt{3} \times \sqrt{3}$	$L1 \leftrightarrow U1$	3(b)	−50
$p = 1$ [201]		See $p = 1$ [001]			
$p = 2$ [201]	$\frac{1}{2}$	4×1	$(L1, L2) \leftrightarrow (U3, U4)$	4(b)	−5.6
$p = 3$ [201]	$\frac{1}{2}$	1×4	$(L1, L2) \leftrightarrow (U1, U4)$	4(c)	−2.7

TABLE V. Formation energies and band gaps for GaP/InP SL's from first-principles pseudopotential calculations, using the local-density approximation (LDA). VFF formation energies are listed for comparison. The band gaps are uncorrected LDA values. The LDA calculated band gaps are 1.55 eV for GaP (indirect) and 0.94 eV for InP. The corresponding experimental band gaps are 2.24 and 1.27 eV.

				ΔH (meV per four-atom unit)		
G	p	Unit cell	Atoms swapped	LDA	VFF	E_g (eV)
[001] abrupt	1			101	81	1.26
[001]	1	4×1	$(L1, L2)(U1, U2)$	73	70	1.33
[111] abrupt	1			156	124	0.98
[111]	1	$\sqrt{3} \times \sqrt{3}$	$L1U1$	68	68	1.36
[111]	1	$\sqrt{3} \times \sqrt{3}$	$L1U2$	76	70	1.32
[111]	1	2×2	$(L1, L3)(U1, U3)$	73	71	1.38
[111]	1	2×2	$(L1, L3)(U1, U3)$	73	72	1.40

constructed structure (Fig. 6) can also be viewed as a $p = 3$ SL in the [135] direction. There are also several other reconstructions whose formation energy is almost as low (Table V). Thus the bulk CuPt structure is unstable not only with respect to *global* phase separation and randomization,[7] but it is also highly unstable with respect to local atomic changes. In contrast, at the free surface, the CuPt structure of $\mathrm{GaInP_2}$ is the most stable low-energy structure.[13,14]

To understand the trends in the reconstructions, we first analyze the formation energies of abrupt GaP/InP SL's, as a function of orientation **G** and repeat period p. The formation enthalpy (per four-atom unit) of the abrupt (A) SL's with $p \geq 3$ can be written in the form[7]

$$\Delta H_A(p, \mathbf{G}) = \Delta E_{\mathrm{CS}}(\mathbf{G}) + \frac{2I(\mathbf{G})}{p}, \tag{2}$$

where ΔE_{CS} is the constituent strain energy, which is equal to the energy of the $p \to \infty$ SL. ΔE_{CS} is the average energy of GaP and InP constrained to the SL lattice constant in the plane perpendicular to **G** and relaxed in the **G** direction. For GaP/InP we find from VFF calculations that

$$\Delta E_{\mathrm{CS}}(001) = 88, \quad \Delta E_{\mathrm{CS}}(011) = 114,$$
$$\Delta E_{\mathrm{CS}}(111) = 122, \quad \Delta E_{\mathrm{CS}}(201) = 103, \tag{3}$$

in units of meV per four-atom unit. It follows that the order of stability for long-period SL's is $[001] < [201] < [011] < [111]$.

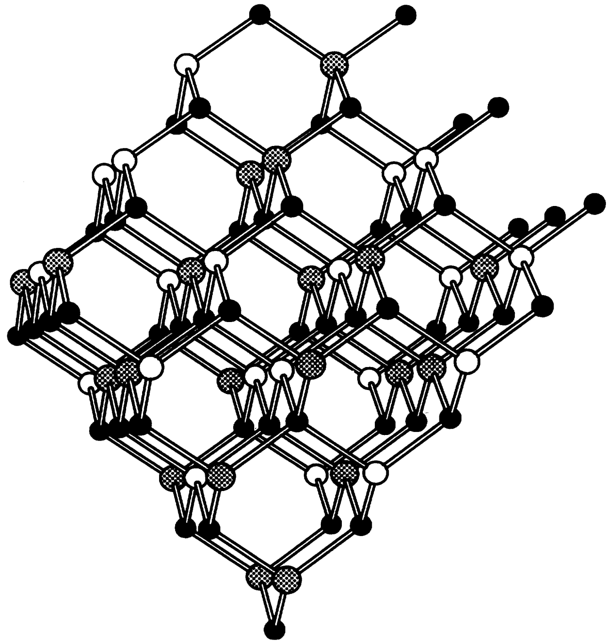

FIG. 6. Lowest-energy reconstructed structure of the $p = 1$ GaP/InP [111] SL. This structure is a $p = 3$ SL in the [135] direction. The white, shaded, and solid atoms are Ga, In, and P, respectively.

The second term in Eq. (2) gives the effects of the two interfaces per unit cell on the formation enthalpy. Applying Eq. (2) to the VFF results, we find, in units of meV per interface unit,

$$I(001) = -3, \quad I(011) = -35,$$
$$I(111) = +1, \quad I(201) = -47 \tag{4}$$

for the interfacial energies of abrupt long-period SL's. Clearly, SL's in the [201] and [011] directions have large, negative interface energies because the atoms near the interface experience massive strain-relieving relaxations. These relaxations are made possible by the low symmetry of the atoms at the interface: three out of four bonds at the [011] interface are symmetry inequivalent, while all bonds at the [201] interface are inequivalent. By contrast, abrupt SL's in the [001] and [111] directions have only two types of symmetry inequivalent bonds, which reduces the scope for relaxation.

Interface reconstructions can change only the interface energy I, not the strain energy ΔE_{CS}. Since the reconstructed (R) SL's that we examine have one abrupt interface and one reconstructed interface per unit cell, we write its formation enthalpy as

$$\Delta H_R(p, \mathbf{G}) = \Delta E_{\mathrm{CS}}(\mathbf{G}) + \frac{I(\mathbf{G})}{p} + \frac{J(\mathbf{G})}{p}, \tag{5}$$

where $J(\mathbf{G})$ is interface energy of the *reconstructed* interface, and $I(\mathbf{G})$ is taken from Eq. (2) for the abrupt SL. From Eqs. (2) and (5), we have

$$\Delta(p, \mathbf{G}) \equiv \Delta H_R(p, \mathbf{G}) - \Delta H_A(p, \mathbf{G}) = \frac{J(\mathbf{G}) - I(\mathbf{G})}{p}, \tag{6}$$

as the energy lowering due to reconstruction, which depends only on the interfacial energies. Using Eq. (5), the values of $J(\mathbf{G})$ in (meV per interface unit) for the lowest energy reconstructions are

$$J(001) = -14, \quad J(011) = -62,$$
$$J(111) = -49, \quad J(201) = -48. \tag{7}$$

Comparing these results with Eq. (4), we see that the [001] and [111] interfaces, which are nonrelaxing when they are abrupt, now become strongly relaxing when they are reconstructed.

The effect of the reconstruction on ΔH is small for longer-period SL's because ΔH is dominated by the strain energy of the atoms far from the interface (ΔE_{CS}). For the atoms near the interface, however, the energy gain due to reconstruction is $I - J$, which is just as large for long-p SL's as for short. Thus the *local* energetics favor interface reconstruction for all periods, even though the reconstruction decreases the *global* ΔH by only a small amount.

We can understand which reconstructions are most energy lowering by examining the distribution of nearest neighbors around each P atom. The nearest neighbors of each P atom form a cation tetrahedron, whose vertices consist of one of In_4, Ga_1In_3, Ga_2In_2, Ga_3In_1, or Ga_4. *The common feature of the lowest energy reconstructions is that they have only mixed tetrahedra* (that is, they have no In_4 or Ga_4 tetrahedra). The reason for this is that mixed tetrahedra allow the central P atom to relax in the direction of the Ga atom(s). This provides effective strain relief because the relaxed Ga-P bonds and In-P bonds are close to their preferred bond lengths. The highly symmetric pure tetrahedra, on the other hand, have little scope for bond relaxation, since the central P atom is surrounded by four atoms of the same type. The lowest-energy structure of all of the GaP/InP SL's is the $p = 2$ [201] SL (chalcopyrite structure) which has only Ga_2In_2 tetrahedra; this structure also has the lowest interface energy, I [Eq. (2)]. For this structure, there are no energy-lowering reconstructions.

Bernard[26] has calculated the energy of the random alloy by averaging over many randomly generated configurations of $GaInP_2$ in a 1000 atom supercell, with all atomic positions relaxed. Within the VFF model, he finds $\Delta H = 82$ meV per four-atom unit for the random alloy. Comparing this number with the results of Table III, we see that for short-period SL's, in particular [001] SL's with $p \leq 3$ and the $p = 1$ [111] SL, the reconstructed SL's are stable with respect to the random alloy, while the abrupt SL's are not. (Of course at high temperatures entropy will favor the random alloy.)

A striking feature of these reconstructions is the relationship between ΔH and the band gap—the structures that have the smallest ΔH also have the largest band gap (Table V). From an electronic point of view, the most favorable swaps are those that lower the energy of the valence-band states. Hybertsen[4] and Dandrea *et al.*[6] find that reconstruction does not affect the *band offset* of common-atom semiconductor SL's. Their results, however, apply to longer-period SL's, while our results for the band gap are for monolayer SL's, where the band offset is not well defined.

Because of the importance of the size difference between In and Ga, the InP/GaP results depend on the substrate on which the materials are grown. The results presented above are for GaP/InP SL's at their equilibrium lattice constant, which is approximately the lattice constant of GaAs. When the SL is grown on either InP ($a_L = 5.87$ Å) or GaP ($a_L = 5.45$ Å), $\Delta E_{\rm CS}$, and hence ΔH, increases. The SL's grown on InP have the largest formation energies (Table VI). This is because all of the strain is now in the GaP layers, and the Ga-P bonds are stiffer than the In-P bonds.[20] This also explains why reconstruction is more favorable at large substrate lattice constants than at small ones. Table VI shows that the SL's grown on InP are very unstable with respect to reconstruction. The abrupt, long p, interfacial energies are

$$I(001) = -4, \quad I(011) = -63,$$
$$I(111) = -1, \quad I(201) = -103 \qquad (8)$$

for abrupt SL's, while for reconstructed SL's they are, in meV per interface unit

$$J(001) = -84, \quad J(011) = -147,$$
$$J(111) = -111, \quad J(201) = -152. \qquad (9)$$

The only SL that is stable with respect to reconstruction when grown on InP is the $p = 2$[201] SL (the chalcopyrite

TABLE VI. VFF predictions for the lowest-energy reconstructions of GaP/InP SL's grown on InP. The reconstructions are, for [001] 2×2 $(L1, L2)$ swapped with $(U1, U4)$ for $p = 1$ [Fig. 1(c)], and $\sqrt{2} \times \sqrt{2}$ $L1$ swapped with $U1$ for $p \geq 2$ [Fig. 1(a)]. The reconstructions for [011] are 4×1 $(L1, L2)$ swapped with $(U1, U2)$ for $p = 1$ [Fig. 2(c)], and 3×1 $(L1, L2)$ swapped with $(U1, U2)$ for $p \geq 2$ [Fig. 2(a)]. The reconstructions for [111] are $\sqrt{3} \times \sqrt{3}$ $L1$ swapped with $U1$ for all p [Fig. 3(b)]. The reconstructions for [201] are 4×1 $(L1, L2)$ swapped with $(U1, U2)$ for $p = 1$ [Fig. 4(b)], and 1×3 $(L1, L2)$ swapped with $(U1, U2)$ for $p \geq 3$ [Fig. 4(a)]. A blank entry for reconstructed means that all reconstructions raised the SL energy. Here the $p = 1$ SL's are all different because they are constrained to the substrate in different planes.

	ΔH (meV per four-atom unit) for period p					
G	$p = 1$	$p = 2$	$p = 3$	$p = 4$	$p = 5$	$p = 6$
[001]						
Abrupt	231	235	236	237	237	237
Reconstructed	181	195	209	217	221	224
[011]						
Abrupt	212	238	266	276	282	286
Reconstructed	190	213	234	255	265	272
[111]						
Abrupt	325	327	327	327	327	327
Reconstructed	216	273	291	300	306	309
[201]						
Abrupt	209	186	222	235	246	251
Reconstructed	197		201	224	233	243

TABLE VII. VFF predictions for the lowest-energy reconstructions of GaP/InP SL's grown on GaP. No energy-lowering reconstructions were found for [001] SL's. The reconstructions for [011] are 4×1 $(L1, L2)$ swapped with $(U1, U2)$ for $p = 1$ and $p = 3$ [Fig. 2(c)]. The reconstructions for [111] are $\sqrt{3} \times \sqrt{3}$ $L1$ swapped with $U2$ for $p = 1$ [Fig. 3(b)], and 4×1 $(L1, L2)$ swapped with $(U2, U3)$ for $p \geq 2$ [Fig. 3(c)]. The reconstruction for [201] is 4×1 $(L1, L2)$ swapped with $(U1, U2)$ for $p = 1$ [Fig. 4(b)]. A blank entry for reconstructed means that all reconstructions raised the SL energy. Here the $p = 1$ SL's are all different because they are constrained to the substrate in different planes.

	ΔH (meV per four-atom unit) for period p					
G	$p=1$	$p=2$	$p=3$	$p=4$	$p=5$	$p=6$
[001]						
Abrupt	133	136	137	137	137	138
[011]						
Abrupt	203	158	172	172	174	175
Reconstructed	194		168			
[111]						
Abrupt	198	196	195	194	194	194
Reconstructed	178	187	189	190	190	191
[201]						
Abrupt	187	147	150	156	159	158
Reconstructed	169					

structure).

For SL's grown on GaP (Table VII), the situation is reversed. Here the change in lattice constant makes the SL's more stable with respect to reconstruction, even though the formation enthalpy is increased. The interface energies for the abrupt SL's grown on GaP are

$$I(001) = -3, \quad I(011) = -15, \quad I(111) = +2, \quad I(201) = -25 \tag{10}$$

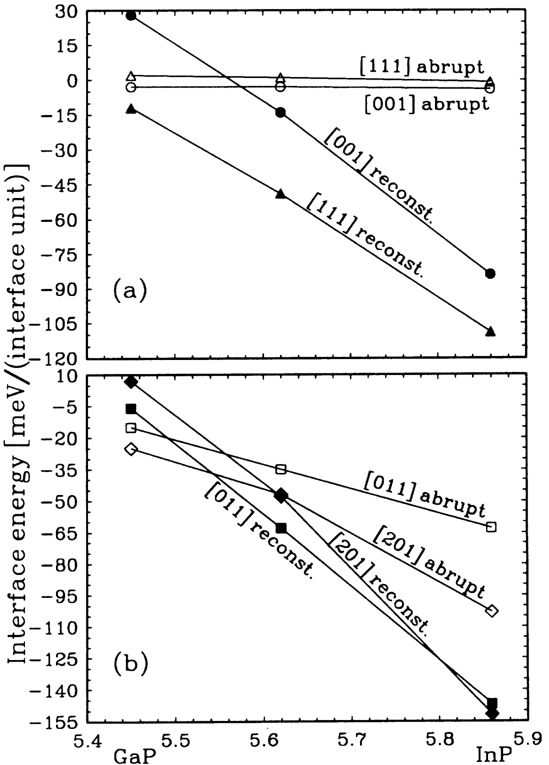

FIG. 7. Interface energies, drawn from data for $p \geq 3$, of abrupt (open symbols) and reconstructed (filled symbols) SL's as a function of the substrate lattice constant. For each direction, a consistent reconstruction (the lowest-energy reconstruction at the equilibrium lattice constant, as in Table IV) is used, even though it is not always the lowest-energy reconstruction for the GaP substrate. (a) shows the results for [001] and [111] SL's, which are nonrelaxing when abrupt, but relaxing when reconstructed. (b) shows the results for the strongly relaxing [011] and [201] SL's. Here the effects of reconstruction are smaller.

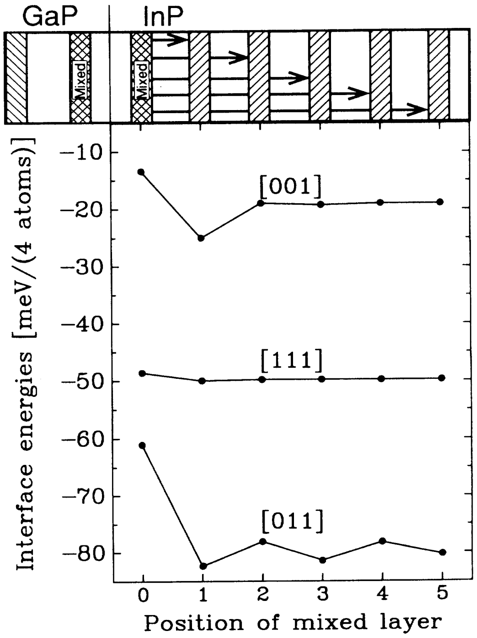

FIG. 8. Reconstructed interface energy as the mixed layer on the InP side moves into the interior of the InP region, while the mixed layer on the GaP side remains adjacent to the interface. The value of 0 corresponds to the normal case of a reconstructed interface as defined in the text.

and

$$J(111) = -16 \tag{11}$$

for the reconstructed SL's. There are no energy-lowering reconstructions for long-period SL's in the [001], [011], and [201] directions. For large p, where the $\Delta H = \Delta E_{\rm CS}$, the universal ordering of [001] < [201] < [011] < [111] remains unchanged. Figure 7 plots I and J for long-period SL's, as a function of the substrate lattice constant. $I(001)$ and $I(111)$, which are nonrelaxing, do not change as a function of the lattice constant. Both I and J follow the same trend: they are most energy lowering for the largest lattice constant and the least energy lowering for the smallest lattice constant. We conclude that abrupt GaP/InP SL's are best grown on a smaller substrate.

The swaps described above are limited to the first layer on each side of the interface. To gain further insight into the process of atomic diffusion in superlattices, we examined what happens as the reconstructed layer is moved away from the interface into the bulk region of the SL. We moved the reconstructed layer on one side of the interface towards the bulk (either into the GaP or the InP region), while keeping the other layer fixed at the interface. Figures 8 and 9 show the results for SL's grown along the [001], [011], and [111] directions, using SL's with period 10 and the lowest-energy reconstruction for each as described above. When the mixed layer is moved one to two layers from the interfaces, the change in the interfacial energy, J [Eq. (5)], is a complicated function of the local geometry, and no consistent trends emerge. But once the mixed layer moves three or more layers from the interface, the total energy converges rapidly. The universal trends here are that (i) it is easier to move the mixed layer into the InP region than into the GaP region. (ii) Moving one mixed layer away from the interface into the InP region is energetically favored over keeping both mixed layers at the interface. Moving one mixed layer into the GaP region lowers the energy only for [011] SL's. While conservation of atoms requires that the degree of intermixing be the same on both sides of the SL, these results suggest that the Ga atoms that diffuse into the InP region of the SL may be more widely dispersed than the In atoms in the GaP region.

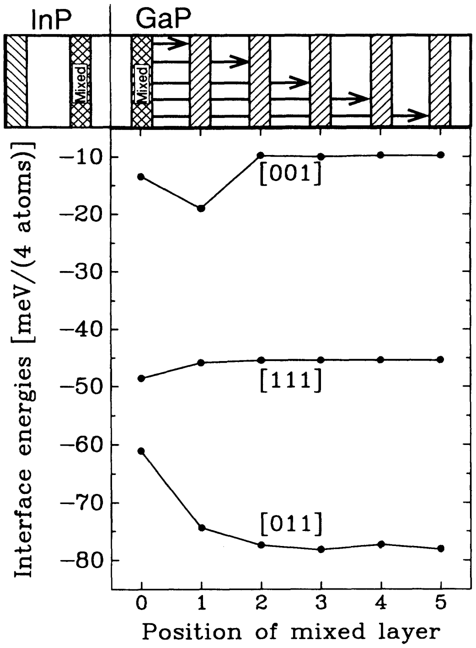

FIG. 9. Reconstructed interface energy as the mixed layer on the GaP side moves into the interior of the GaP region, while the mixed layer on the InP side remains adjacent to the interface. The value of 0 corresponds to the normal case of a reconstructed interface as defined above.

V. SUMMARY

We have compared SL's with abrupt interfaces to those whose interfaces are broadened by reconstruction. For lattice-matched AlAs/GaAs SL's, reconstruction is favorable only for very short periods ($p = 1, 2$), while longer period SL's are found to be stable with respect to reconstruction. Reconstruction is most effective for the $p = 1$ [001] SL (CuAu-like structure), where the energy is lowered from 14 to 4 meV per four-atom unit. For lattice-mismatched GaP/InP SL's, reconstruction can produce large lowering of the interface energy even for long periods. The tendency to reconstruction depends on the direction of the SL, being the largest for the [111] direction. While the abrupt $p = 1$ [001] and $p = 1, 2$ [111] SL's are less stable than the random alloy, their reconstructed SL's are more stable than the random alloy. The abrupt $p = 1$ [111] and $p = 1, 2$ [001] SL's are less stable than the random alloy, while after reconstruction they are more stable than the random alloy. The substrate lattice constant on which the SL is grown strongly affects the reconstruction: perfectly abrupt interfaces are most stable on a small substrate lattice constant, even though this increases the formation energy of the SL as a whole. For the monolayer SL, reconstruction causes a large increase in the SL band gap compared to the abrupt case.

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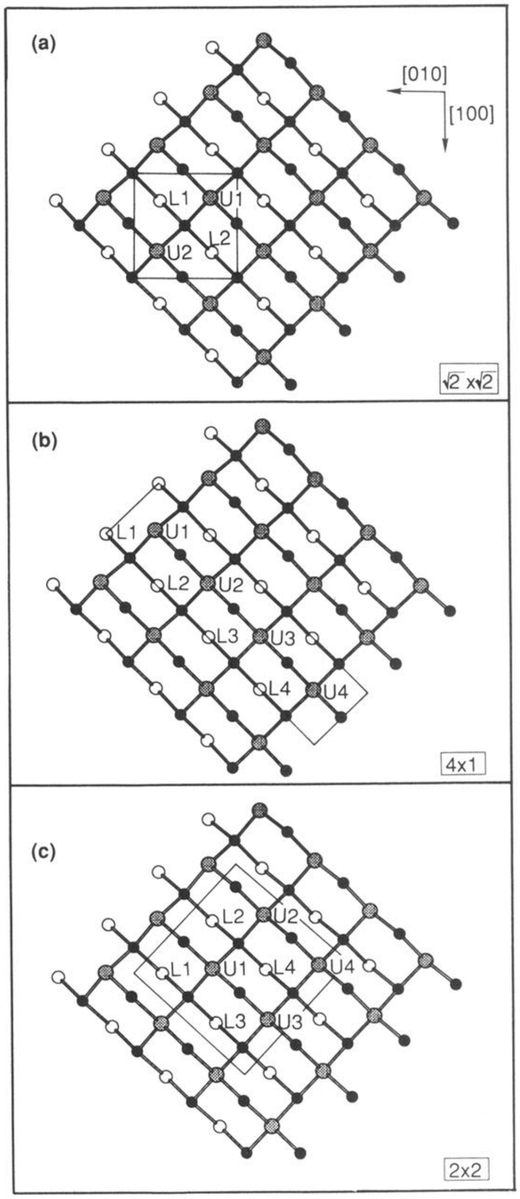

FIG. 1. Some of the unit cells for reconstructions of [001] SL's. For AlAs/GaAs SL's, the white, shaded and solid atoms represent Al, Ga and As, respectively. For GaP/InP, the corresponding identifications are Ga, In, and P.

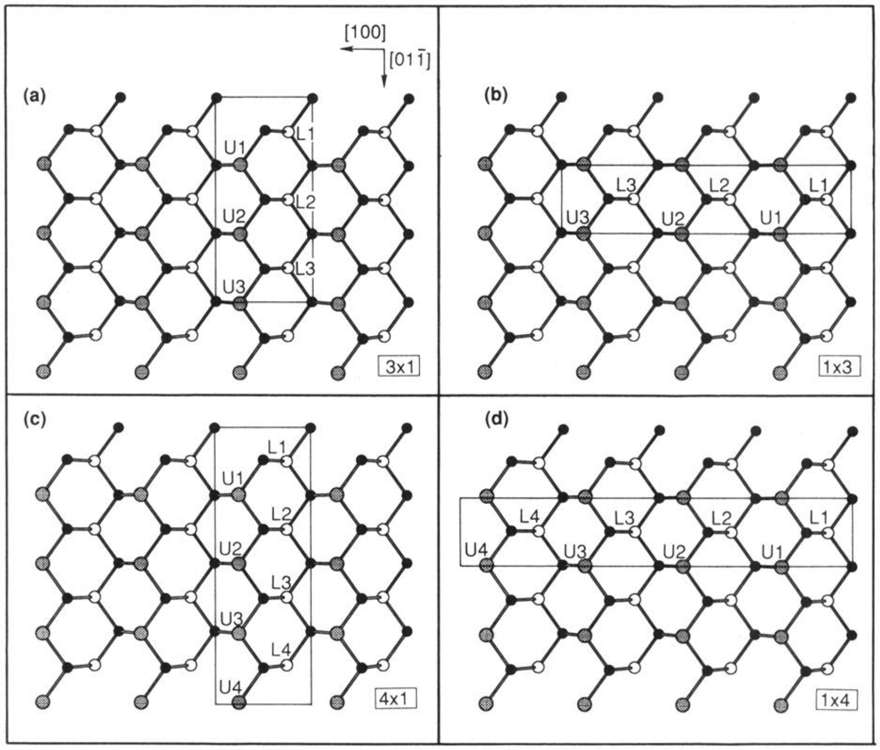

FIG. 2. Some of the unit cells for reconstructions of [011] SL's. Identifications of atoms are the same as in Fig. 1.

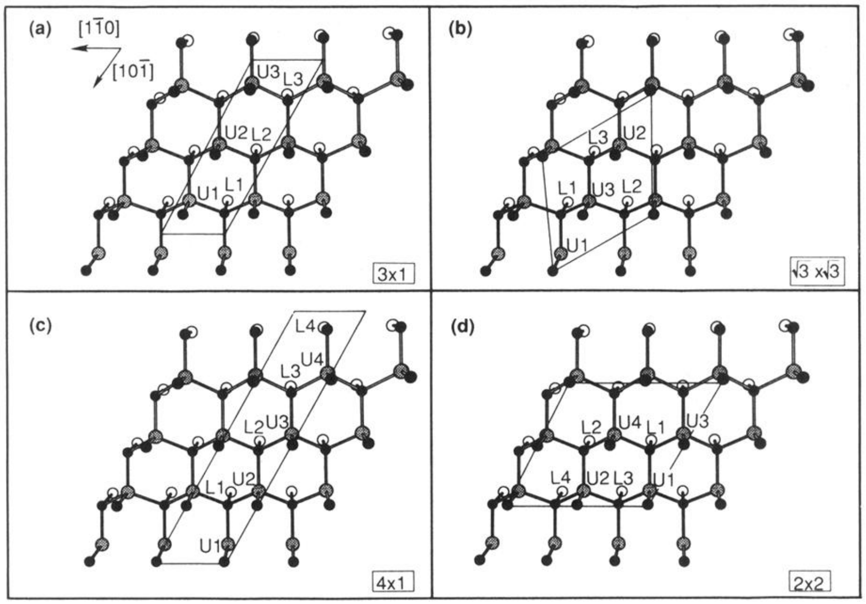

FIG. 3. Some of the unit cells for reconstructions of [111] SL's. Identifications of atoms are the same as in Fig. 1.

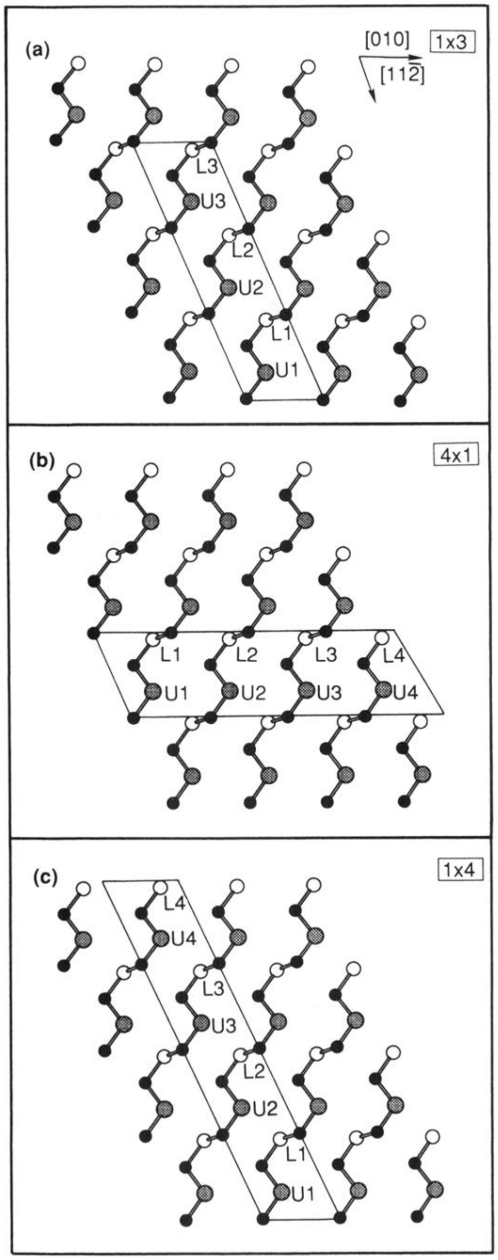

FIG. 4. Some of the unit cells for reconstructions of [201] SL's. Identifications of atoms are the same as in Fig. 1.

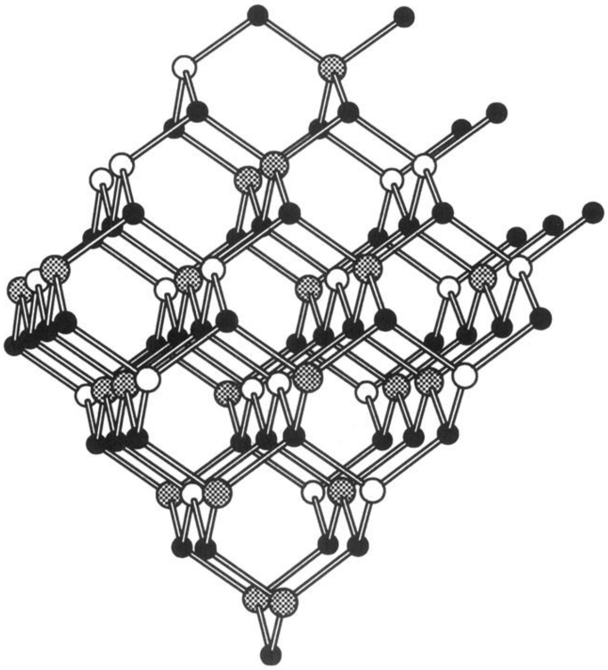

FIG. 6. Lowest-energy reconstructed structure of the $p = 1$ GaP/InP [111] SL. This structure is a $p = 3$ SL in the [135] direction. The white, shaded, and solid atoms are Ga, In, and P, respectively.