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Stability of the $(InAs)_1/(GaAs)_1$ monolayer superlattice

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A first-principles total-energy pseudopotential calculation has been performed for the (001) $(InAs)_1/(GaAs)_1$ monolayer superlattice. It is shown that bulk $(InAs)_1/(GaAs)_1$ is thermodynamically unstable with respect to disproportionation into zinc-blende constituents. This instability is attributed to the unfavorable charge transfer from the GaAs layers to the InAs layers by estimating the strain-related and chemical contributions to the superlattice formation energy. It is found that epitaxial $(InAs)_1/(GaAs)_1$ grown on InAs, InP, or GaAs substrate is much less unstable than bulk $(InAs)_1/(GaAs)_1$, since the strain-related contribution becomes negative due to the epitaxial constraints. A simple criterion for the direction of charge transfer in monolayer superlattices is also proposed.

I. INTRODUCTION

Remarkable recent progress in thin-film growth techniques, such as molecular-beam epitaxy (MBE) and metalorganic chemical-vapor deposition (MOCVD), has made it possible to control epitaxial growth to almost one monolayer.[1] Using these techniques, it is now possible to make ultrathin layered semiconductor superlattices with sharp interfaces, opening up possibilities for new devices.

The stability of the obtained artificial materials is an important problem from the standpoints of crystal growth and device application. The report of successful growth of $(GaAs)_1/(AlAs)_1$ monolayer superlattices[2] was surprising because GaAs layers and AlAs layers were expected to be fully miscible at MBE growth temperatures.[3] Phillips[4] suggested that this monolayer superlattice was intrinsically unstable but stabilized due to pinning by oxygen impurities incorporated during the growth. On the other hand, Kuan *et al.*[5] have recently observed an ordered $(GaAs)_1/(AlAs)_1$ phase in continuous growth from $Ga_{0.5}Al_{0.5}As$ alloys, and characterized it as a thermodynamic equilibrium phase of $Ga_xAl_{1-x}As$. Since all disordered (D) isovalent pseudobinary semiconductor alloys are known to have positive mixing enthalpies ΔH^D and to be unstable at low temperatures,[3,6] the observation of long-range order in $Ga_xAl_{1-x}As$ alloys is particularly interesting. Despite extensive study, it has generally not been known whether artificial semiconductor superlattices are thermodynamically stable or metastable.

The enthalpy of formation ΔH^O of a given ordered structure contains two types of contributions. The first one is the contribution due to microscopic strain (MS) $\Delta E_{\rm MS}$, resulting from the deformation of bond lengths and angles occurring during formation of the structure. The second is the chemical (chem) contribution $\Delta E_{\rm chem}$ incorporating actual interaction; i.e., charge transfer, polarization, or formation of new types of bonds. Since the strain energy is positive definite, theories which neglect $\Delta E_{\rm chem}$ necessarily lead to positive ΔH^O.[7] The formation enthalpy ΔH^O is negative only if $\Delta E_{\rm chem}$ is negative and overwhelms positive $\Delta E_{\rm MS}$.

The evaluation of this $\Delta E_{\rm chem}$ requires a quantum-mechanical calculation. Several calculations have recently been performed. The first-principles pseudopotential[8-10] and all-electron[8] total-energy calculations for $(GaAs)_1/(AlAs)_1$ have shown that the chemical contribution $\Delta E_{\rm chem}$ is positive and that the superlattice is thermodynamically unstable. According to these calculations, electrons are transferred from the AlAs layers to the GaAs layers. The cohesive energy of AlAs is known to be larger than that of GaAs.[8,11] Therefore, this charge transfer from the more stable layers (AlAs) to the less stable layers (GaAs) results in positive $\Delta E_{\rm chem}$. On the other hand, Srivastava *et al.*,[12] using the first-principles pseudopotential method, have shown that the $(InP)_1/(GaP)_1$ monolayer superlattice is the thermodynamically stable low-temperature ground state. In this case, the direction of charge transfer, which is from the InP layers to the GaP layers, coincides with increased cohesion. The resulting negative $\Delta E_{\rm chem}$ overwhelms positive $\Delta E_{\rm MS}$ and leads to negative enthalpy ΔH^O. The chemical contribution $\Delta E_{\rm chem}$ which is closely related to the charge transfer, plays an important role in determining the stability of superlattices. However, it is not yet clear whether the charge transfer is from a less stable layer to a more stable layer or vice versa.

The InAs/GaAs lattice-mismatched superlattices have recently attracted much attention because of the possibilities of tailoring band gaps,[13] fabricating new devices,[14] and decreasing the random alloy scattering of electrons.[15] Successful growths of the $(InAs)_1/(GaAs)_1$ monolayer superlattice[16] and the ultrathin layered superlattice[17] using MOCVD and MBE techniques have been reported. Furthermore, the observation of long-range order in the $In_{0.5}Ga_{0.5}As$ alloy has been reported.[18] Although the electronic properties of these superlattices have been investigated by the semiempirical pseudopotential method,[19] there is no accurate calculation for the stability of superlattice structures. It is particularly interesting to compare the stability of $(InAs)_1/(GaAs)_1$ with that of $(InP)_1/(GaP)_1$, which is predicted to be thermodynamically stable.

In the present paper we have studied the stability of the $(\mathrm{InAs})_1/(\mathrm{GaAs})_1$ monolayer superlattice in the (001) orientation using the first-principles total-energy pseudopotential method. The stabilities of both bulk-grown and epitaxially grown superlattices are examined. The effect of the epitaxial constraints is clarified. Estimations are made of the microscopic strain contribution and the chemical contribution to the enthalpy of formation. The effect of the chemical contribution is discussed. In addition a simple criterion for the direction of charge transfer in III-V compound semiconductor monolayer superlattices is presented.

II. CALCULATION METHODS

We employ the first-principles total-energy pseudopotential method[20] within the local-density-functional (LDF) formalism. As for the pseudopotential, we use the semirelativistic norm-conserving pseudopotentials of Bachelet *et al.*,[21] which are constructed in the relativistic all-electron calculation of atomic energy levels and wave functions within the LDF formalism. The Wigner form[22] is adopted for the exchange correlation energy in the local-density approximation. Self-consistency is achieved within 0.01 meV for the mean difference between the input and the output crystal potentials. The wave functions are expanded in terms of a plane-wave basis set. We adopt the plane waves such that $|\mathbf{k}+\mathbf{G}| \leq 3.6$ a.u. as a basis. This corresponds to about a 500–plane-wave basis for the $(\mathrm{InAs})_1/(\mathrm{GaAs})_1$ monolayer superlattice. Twelve special points are adopted in the integration over the Brillouin zone. Fourier transformation is performed using about 8000 mesh points in the unit cell of $(\mathrm{InAs})_1/(\mathrm{GaAs})_1$. To assure the relative energy difference between the monolayer superlattice and its zinc-blende constituents, the calculation for InAs and GaAs is performed in the tetragonal unit cell of a monolayer superlattice structure.

In Table I we list the calculated equilibrium lattice constants and bulk moduli on InAs and GaAs. The calculated values are in good agreement with experimental values.[23,28] The calculated lattice mismatch between InAs and GaAs is 18% smaller than the experimental value. The first-principles calculation for $(\mathrm{InAs})_1/(\mathrm{GaAs})_1$ may underestimate by about 30% the strain energy due to the lattice mismatch.

TABLE I. Calculated lattice constants and bulk moduli for InAs and GaAs.

	InAs		GaAs	
	Calc.	Expt.	Calc.	Expt.
Lattice constant (Å)	5.905	6.058[a]	5.572	5.653[a]
Bulk modulus (Mbar)	0.64		0.87	0.79[b]

[a]Reference 23.

[b]Reference 24.

While both InAs and GaAs have a zinc-blende structure, the $(\mathrm{InAs})_1/(\mathrm{GaAs})_1$ monolayer superlattice has a tetragonal structure. The tetragonal primitive cell is characterized by the lattice parameters a and c (where we define the tetragonal ratio $\eta = c/a$) and the As atom displacement parameter u, which is the interlayer distance between the In layer and the As layer measured in units of c. In a $(\mathrm{InAs})_1/(\mathrm{GaAs})_1$ structure, the In—As bond length R_{InAs} and the Ga—As bond length R_{GaAs} are given by

$$\begin{aligned} R_{\mathrm{InAs}} &= a\left(\tfrac{1}{8} + \eta^2 u^2\right)^{1/2} , \\ R_{\mathrm{GaAs}} &= a\left[\tfrac{1}{8} + \eta^2 (u - \tfrac{1}{2})^2\right]^{1/2} . \end{aligned} \tag{1}$$

When $\eta = 1$ and $u = 0.25$, we have $R_{\mathrm{InAs}} = R_{\mathrm{GaAs}}$. These bond lengths are generally different from the bulk bond lengths of InAs and GaAs. Then, the superlattice has the finite strain energy due to the distortion of bond lengths and bond angles.

The total energy of the superlattice is a function of the three structural parameters a, η, and u, which is denoted as $E(a,\eta,u)$. It would take much computational time to precisely find the energy-minimizing equilibrium values of these parameters using the self-consistent first-principles method. Here we adopt Keating's valence-force-field (VFF) method[25] to find the equilibrium geometries. Since the VFF method neglects chemical energy, it cannot evaluate the formation enthalpy correctly. However, it is pointed out[12,26] that chemical energy has a negligible effect on the position of its minimum; that is, the equilibrium geometries can be decided with useful accuracy by the VFF method. Thus, we determine the equilibrium geometry from the VFF method, and then calculate the total energy for the obtained geometry using the self-consistent first-principles method.

III. RESULTS AND DISCUSSION

A. Bulk phases

The enthalpy of formation of a bulk $(\mathrm{InAs})_1/(\mathrm{GaAs})_1$ monolayer superlattice is defined as its equilibrium total energy relative to the energy of its constituents InAs and GaAs at their respective equilibria:

$$\begin{aligned} \Delta H^{o} = {} & E((\mathrm{InAs})_1/(\mathrm{GaAs})_1, a_{\mathrm{eq}}, \eta_{\mathrm{eq}}, u_{\mathrm{eq}}) \\ & - E(\mathrm{InAs}, a_{\mathrm{InAs}}) - E(\mathrm{GaAs}, a_{\mathrm{GaAs}}) . \end{aligned} \tag{2}$$

Here, all structural parameters attain their energy-minimizing equilibrium values. The values of a_{InAs} and a_{GaAs} are obtained by the first-principles method. The values of a_{eq}, η_{eq}, and u_{eq} are determined by the VFF method with the obtained theoretical InAs and GaAs bond lengths. The values of the structural parameters used in the first-principles total-energy calculations and the calculated total energies are listed in Table II. From the lines labeled Ia in Table II, we find that $\Delta H^{o} = 60.1$ meV, which is listed in Table III. This value is very close to that obtained using the low-order perturbation theory concerning uniform electron gas (50.1 meV).[27] The positive ΔH^{o} indicates that bulk $(\mathrm{InAs})_1/(\mathrm{GaAs})_1$ is unstable with respect to disproportionation into zinc-blende constituents. Since there is a large lattice mismatch between InAs and GaAs, the disordered phase is expected to have a higher formation enthalpy than the ordered structure. This is because the variety of local atomic environments in the disordered phase does not accommodate the distinct bond lengths and angles as well as does the ordered

TABLE II. Calculated total energies E of $(\mathrm{InAs})_1/(\mathrm{GaAs})_1$, InAs, and GaAs, along with the used structural parameters a, η, and u.

	Label	a (Å)	η	u	E (Ry)	Conditions
$(\mathrm{InAs})_1/(\mathrm{GaAs})_1$	Ia	5.701	1.015	0.266	−34.096 255	Bulk, $a=a_{\mathrm{eq}}$
	Ib	5.701	1	0.25	−34.087 769	Unrelaxed
	II	5.905	0.943	0.266	−34.092 313	Epitaxial on InAs
	III	5.701	1.015	0.266	−34.096 255	Epitaxial on InP
	IV	5.572	1.062	0.266	−34.092 757	Epitaxial on GaAs
InAs	Ia	5.905	1		−33.709 888	Bulk
	Ib	5.701	1		−33.691 234	$a=a_{\mathrm{eq}}$, $\eta=1$
	II	5.905	1		−33.709 888	Epitaxial on InAs
	III	5.701	1.076		−33.704 448	Epitaxial on InP
	IV	5.572	1.125		−33.695 288	Epitaxial on GaAs
GaAs	Ia	5.572	1		−34.491 465	Bulk
	Ib	5.701	1		−34.485 639	$a=a_{\mathrm{eq}}$, $\eta=1$
	II	5.905	0.887		−34.476 281	Epitaxial on InAs
	III	5.701	0.955		−34.489 052	Epitaxial on InP
	IV	5.572	1		−34.491 465	Epitaxial on GaAs

phase having a single type of local bond configuration.[12] Therefore, once constructed, the ordered $(\mathrm{InAs})_1/(\mathrm{GaAs})_1$ will persist metastably on a laboratory time scale because of activation barriers for decomposition posed by coherent strain effects[28] and insufficient diffusivity. The first-principles study for $(\mathrm{InP})_1/(\mathrm{GaP})_1$ has predicted that ΔH^{O} is negative and that this structure is thermodynamically stable. Why very similar superlattices $(\mathrm{InAs})_1/(\mathrm{GaAs})_1$ and $(\mathrm{InP})_1/(\mathrm{GaP})_1$, are different in stability is an intriguing question.

We analyze the physical mechanisms behind this instability ($\Delta H^{O}=60.1$ meV) by imaging formation of $(\mathrm{InAs})_1/(\mathrm{GaAs})_1$ which occurs in three conceptual steps.[12] In the first step we compress a_{InAs} and dilate a_{GaAs} to the equilibrium lattice constant a_{eq} of $(\mathrm{InAs})_1/(\mathrm{GaAs})_1$. This step requires a volume deformation (VD) energy

$$\Delta E_{\mathrm{VD}}=E(\mathrm{InAs},a_{\mathrm{eq}})+E(\mathrm{GaAs},a_{\mathrm{eq}})-E(\mathrm{InAs},a_{\mathrm{InAs}})-E(\mathrm{GaAs},a_{\mathrm{GaAs}}) \; . \tag{3}$$

The first-principles calculations, the results of which are listed in the Ia and Ib lines of Table II, yield $\Delta E_{\mathrm{VD}}=166.5$ meV. This energy is positive since this step induces the deformation of equilibrium structures. In the second step we bring the prepared (compressed or dilated) InAs and GaAs unit together to form an $(\mathrm{InAs})_1/(\mathrm{GaAs})_1$ superlattice structure, without relaxing the bond lengths and angles to their equilibrium values (i.e., retrain $\eta=1$ and $u=0.25$). This step requires an energy change:

$$\Delta E_{\mathrm{CE}}=E((\mathrm{InAs})_1/(\mathrm{GaAs})_1,a_{\mathrm{eq}},\eta=1,u=0.25)-E(\mathrm{InAs},a_{\mathrm{eq}})-E(\mathrm{GaAs},a_{\mathrm{eq}}) \; , \tag{4}$$

due to possible charge exchange (CE) between atoms, which is found to be 9.1 meV (see Table II). In the final step we relax the geometry of $(\mathrm{InAs})_1/(\mathrm{GaAs})_1$ to achieve equilibrium, involving a structural (S) energy

$$\Delta E_{S}=E((\mathrm{InAs})_1/(\mathrm{GaAs})_1,a_{\mathrm{eq}},\eta_{\mathrm{eq}},u_{\mathrm{eq}})-E((\mathrm{InAs})_1/(\mathrm{GaAs})_1,a_{\mathrm{eq}},\eta=1,u=0.25) \; , \tag{5}$$

which is found to be −115.4 meV (see Table II). The energy ΔE_{S} consists of two contributions: the strain relief (SR) energy ΔE_{SR} of $(\mathrm{InAs})_1/(\mathrm{GaAs})_1$ upon relaxing η and u without charge redistribution, and a residual chemical energy ΔE_{res} associated with relaxation-induced charge rearrangements. We can evaluate ΔE_{SR} by using the VFF method. It is found that $\Delta E_{\mathrm{SR}}=-110.3$ meV and $\Delta E_{\mathrm{res}}=-5.2$ meV. The formation enthalpy ΔH^{O}, the sum of Eqs. (3)–(5), can be written as

$$\Delta H^{O}=(\Delta E_{\mathrm{VD}}+\Delta E_{\mathrm{SR}})+(\Delta E_{\mathrm{CE}}+\Delta E_{\mathrm{res}})=\Delta E_{\mathrm{MS}}+\Delta E_{\mathrm{chem}} \; . \tag{6}$$

In this way we can divide the formation enthalpy ΔH^{O} into the microscopic strain (MS) term ΔE_{MS} reflecting the lattice mismatch between InAs and GaAs, and the chemical term ΔE_{chem} incorporating the charge transfer. For $(\mathrm{InAs})_1/(\mathrm{GaAs})_1$, we have $\Delta E_{\mathrm{MS}}=56.2$ meV and $\Delta E_{\mathrm{chem}}=3.9$ meV. Analysis of the calculated charge distributions has revealed that electrons are transferred from the GaAs layers to the InAs layers. The positive ΔE_{chem} is caused by this charge transfer since the cohesive energy of InAs is known to be smaller than that of GaAs.[11] On the other hand, it is reported[12] that the charge is transferred from the less stable InP layers to the more stable GaAs layers in $(\mathrm{InP})_1/(\mathrm{GaP})_1$. This charge transfer leads to negative ΔE_{chem} which overwhelms positive ΔE_{MS}, and renders the system thermodynamically

TABLE III. Calculated bulk and epitaxial formation enthalpies ΔH^{O} of $(\mathrm{InAs})_1/(\mathrm{GaAs})_1$ per four atoms.

Conditions	ΔH^{O} (meV)
Bulk	60.1
Epitaxial on InAs	10.5
Epitaxial on InP	6.7
Epitaxial on GaAs	8.4

stable. Thus the instability of $(\mathrm{InAs})_1/(\mathrm{GaAs})_1$ is traced to the unfavorable charge trasfer from the more stable GaAs layers to the less stable InAs layers. In this way, the charge transfer plays an important role in determining the stability of superlattice structures. This point will be discussed later.

B. Epitaxial phases

When the $(\mathrm{InAs})_1/(\mathrm{GaAs})_1$ superlattice is grown epitaxially on a substrate (s) of lattice constant a_s without misfit dislocations, its lattice parameter $a_{\parallel}$ parallel to the substrate is constrained to equal a_s. Under such epitaxial conditions, the products (InAs and GaAs) of a disproportionation reaction are also constrained to match a_s in the parallel direction to the substrate, and will be tetragonally distorted. Therefore, the epitaxial formation enthalpy of $(\mathrm{InAs})_1/(\mathrm{GaAs})_1$ grown on a substrate of lattice constant a_s becomes

$$\Delta H^O = E((\mathrm{InAs})_1/(\mathrm{GaAs})_1, a_{\parallel}=a_s) - E(\mathrm{InAs}, a_{\parallel}=a_s) - E(\mathrm{GaAs}, a_{\parallel}=a_s) , \tag{7}$$

where all structural parameters except $a_{\parallel}$ adjust to minimize the energy of each phase. InAs, InP, and GaAs are chosen as substrates. In the case of InP, the value of a_s is assumed to be the equilibrium value of a of bulk $(\mathrm{InAs})_1/(\mathrm{GaAs})_1$, which is expected to nearly equal the theoretical value for InP. In Table II, the results of the VFF estimations of structural parameter η (for tetragonally distorted InAs and GaAs) and of η and u [for $(\mathrm{InAs})_1/(\mathrm{GaAs})_1$] are listed, along with the results of the first-principles total-energy calculations. For InAs as the substrate, for example, we find that GaAs contracts tetragonally to $\eta=0.887$ and $(\mathrm{InAs})_1/(\mathrm{GaAs})_1$ distorts to $\eta=0.943$ and $u=0.266$ (see the lines labeled II in Table II). From the calculated total energies in Table II, it is found that ΔH^O is 10.5, 6.7, and 8.4 meV per four atoms for $(\mathrm{InAs})_1/(\mathrm{GaAs})_1$ on InAs, InP, and GaAs substrates, respectively. These values are much smaller than the value for bulk superlattice (see Table III) but are still positive. It is concluded that the superlattice is thermodynamically unstable in either bulk or epitaxial forms.

In order to clarify the reason for the large reduction in instability, we decompose ΔH^O into the microscopic strain term ΔE_{MS} and the chemical term ΔE_{chem}, similar to the bulk-growth case. The energy ΔE_{MS} is given by

$$\Delta E_{\mathrm{MS}} = E_{\mathrm{VFF}}((\mathrm{InAs})_1/(\mathrm{GaAs})_1, a_{\parallel}=a_s) - E_{\mathrm{VFF}}(\mathrm{InAs}, a_{\parallel}=a_s) - E_{\mathrm{VFF}}(\mathrm{GaAs}, a_{\parallel}=a_s) , \tag{8}$$

where E_{VFF} is the deformation energy of each system, induced by epitaxial constraints. The VFF method predicts ΔE_{MS} to be -4.7, -3.6, and -3.0 meV for InAs, InP, and GaAs substrates, respectively. These values should be compared with $\Delta E_{\mathrm{MS}}=56.2$ meV for the bulk-grown condition. In the case of bulk growth, ΔE_{MS} is necessarily positive since only $(\mathrm{InAs})_1/(\mathrm{GaAs})_1$ has a strain energy and the constituents InAs and GaAs are at their equilibria. Under the epitaxial condition, all of the lattice parameters $a_{\parallel}$ of InAs, GaAs, and $(\mathrm{InAs})_1/(\mathrm{GaAs})_1$ are constrained to equal a_s. Whereas the remaining structural parameter to relieve the strain is only η in InAs and GaAs, two parameters (η and u) can be relaxed to reduce the strain energy. This difference in the degree of freedom between InAs (or GaAs) and $(\mathrm{InAs})_1/(\mathrm{GaAs})_1$ results in negative ΔE_{MS}, which suggests that whenever ΔE_{chem} is negative the epitaxial enthalpy is necessarily negative. The stabilization due to epitaxial constraints is considered to be a general property of a monolayer superlattice with a large lattice mismatch.[29] Subtracting ΔE_{MS} from ΔH^O, we find ΔE_{chem} to be 15.2, 10.3, and 11.4 meV for InAs, InP, and GaAs substrates, respectively. From the calculated charge distributions, it is shown that the charge is transferred from the GaAs layers to the InAs layers in epitaxial $(\mathrm{InAs})_1/(\mathrm{GaAs})_1$ superlattices, as in bulk phases. This charge transfer results in the positive values of ΔE_{chem}, which overwhelm the negative ΔE_{MS}. Thus, the instability of epitaxial $(\mathrm{InAs})_1/(\mathrm{GaAs})_1$ is attributed to the unfavorable charge transfer.

C. Charge transfer

In general, the direction of charge transfer between two different atoms is predicted from their difference in electronegativity; that is, charge is transferred from a less electronegative atom to a more electronegative atom. The electronegativities for a number of atoms have been presented by Phillips;[11] for example, 1.18 (Al), 1.13 (Ga), and 0.99 (In). First-principles calculations[12] have shown that in $(\mathrm{InP})_1/(\mathrm{GaP})_1$ the charge is transferred from the InP layers to the GaP layers, which confirms the prediction of the electronegativity rule. However, the charge transfer from GaAs layers to InAs layers in $(\mathrm{InAs})_1/(\mathrm{GaAs})_1$, as obtained by the present calculations, does not follow this rule. The opposite direction of charge transfer between In and Ga atoms suggests that the direction of charge transfer in $(AC)_1/(BC)_1$ monolayer superlattices cannot be predicted from the difference in an atomic parameter between A and B atoms. Furthermore, the charge transfer from AlAs to GaAs in $(\mathrm{GaAs})_1/(\mathrm{AlAs})_1$ (Ref. 8) does not follow the electronegativity rule either. Then, in order to predict the direction of charge transfer in monolayer superlattices, which is important for their stability, we must find a new criterion.

Recently, Tersoff[30] has proposed the concept of the midgap energy E_B in connection with the problem of the band lineup at semiconductor heterojunctions. The midgap energy E_B of a semiconductor is defined as the energy where the gap states cross over from valence-band to conduction-band character. The first few layers of a semiconductor near an interface have metallic characters because of the presence of a continuum of states in the gap induced by the interface. Then E_B is thought to be the local quasi-Fermi-level in a semiconductor, analogous to the Fermi level in a metal. Simple estimates based on dielectric screening suggest that the midgap energies E_B of two semiconductors are lined up across the interface by the induced interface dipole. Tersoff has calculated,

TABLE IV. Obtained absolute midgap energies E_B for III-V compound semiconductors. Valence-band maximum E_V and midgap energy relative to valence-band maximum, $E_B - E_V$, are also listed. All values are in units of eV.

	E_V [a]	$E_B - E_V$ [b]	E_B
AlP	−10.22	1.27	−8.95
AlAs	−9.67	1.05	−8.62
AlSb	−8.77	0.45	−8.32
GaP	−10.21	0.81	−9.40
GaAs	−9.64	0.70	−8.94
GaSb	−8.77	0.07	−8.70
InP	−10.03	0.76	−9.27
InAs	−9.48	0.50	−8.98
InSb	−8.62	0.01	−8.61

[a] Reference 32.

[b] Reference 30.

directly from the bulk band structures, the positions of E_B with respect to the valence-band maximum E_V for a number of III-V compound semiconductors. His predictions of valence-band discontinuities at various heterojunctions are in good agreement with experimental results.

However, the direction of the induced dipole (i.e., the direction of charge transfer at the interface) cannot be determined from the values of E_B given by Tersoff, since these values are measured relative to E_V of each semiconductor, and not to an absolute energy reference. If the positions of E_B are given with respect to an absolute energy reference, we can predict the direction of charge transfer at the interface: the charge will be transferred from a semiconductor with a higher E_B to that with a lower E_B. Then, the difference in the absolute values of E_B may be a new criterion for the charge transfer at semiconductor heterojunctions. This criterion is thought to be applicable to monolayer superlattices since the transferred charges are strongly localized in the vicinity of the interface.[10,19]

In order to obtain the absolute positions of E_B, we must obtain the positions of the valence-band maximum E_V relative to an absolute energy reference. The regular band calculations for an infinite solid, however, cannot provide any information about such absolute energy positions.[31] An absolute energy scale only enters into the picture if we deal with a semi-infinite crystal terminated by a surface. Complete self-consistent calculations for a surface would be computationally even harder than bulk calculations. Instead, we use the values of E_V obtained by Harrison's tight-binding scheme.[32] These values are derived from atomic information and are thought to be given in effect relative to the vacuum level. As shown in Table IV, we can determine the absolute positions of E_B from the values of E_V, and from the values of E_B relative to E_V, for various III-V compound semiconductors. For $(\mathrm{InAs})_1/(\mathrm{GaAs})_1$, $(\mathrm{InP})_1/(\mathrm{GaP})_1$, and $(\mathrm{GaAs})_1/(\mathrm{AlAs})_1$, the difference in the absolute values of E_B is consistent with the direction of charge transfer obtained from first-principles calculations. Therefore this is a reliable criterion for charge transfer in monolayer superlattices.

TABLE V. Prediction for the chemical contribution ΔE_{chem} to the formation enthalpy of monolayer superlattices. P designates positive ΔE_{chem} and N a negative one.

	ΔE_{chem}		ΔE_{chem}
AlP/GaP	P	AlP/AlAs	N
GaP/InP	N	AlAs/AlSb	N
InP/AlP	P	AlSb/AlP	N
AlAs/GaAs	P	GaP/GaAs	N
GaAs/InAs	P	GaAs/GaSb	N
InAs/AlAs	P	GaSb/GaP	N
AlSb/GaSb	P	InP/InAs	N
GaSb/InSb	N	InAs/InSb	N
InSb/AlSb	P	InSb/InP	N

If the charge is transferred from the less stable layers to the more stable layers, as in $(\mathrm{InP})_1/(\mathrm{GaP})_1$, the chemical term ΔE_{chem} of the formation enthalpy will be negative and will tend to stabilize the system. From the absolute values of E_B and the knowledge of the cohesive energy[11] of III-V compound semiconductors, we can predict whether ΔE_{chem} is negative or positive. The results for various $(A^{\mathrm{III}}C^{\mathrm{V}})_1(B^{\mathrm{III}}C^{\mathrm{V}})_1$ and $(A^{\mathrm{III}}B^{\mathrm{V}})_1/(A^{\mathrm{III}}C^{\mathrm{V}})_1$ monolayer superlattices are listed in Table V. Most $(A^{\mathrm{III}}C^{\mathrm{V}})_1/(B^{\mathrm{III}}C^{\mathrm{V}})_1$ superlattices have positive ΔE_{chem}, which shows that the bulk system is thermodynamically unstable. On the other hand, all $(A^{\mathrm{III}}B^{\mathrm{V}})_1/(A^{\mathrm{III}}C^{\mathrm{V}})_1$ superlattices have negative ΔE_{chem} and seem to be more stable than $(A^{\mathrm{III}}C^{\mathrm{V}})_1/(B^{\mathrm{III}}C^{\mathrm{V}})_1$. In particular, epitaxial forms of $(A^{\mathrm{III}}B^{\mathrm{V}})_1/(A^{\mathrm{III}}C^{\mathrm{V}})_1$ are predicted to be thermodynamically stable since ΔE_{MS} may be negative due to epitaxial constraints. The recent observation[33] of long-range order in $\mathrm{GaAs}_{0.5}\mathrm{Sb}_{0.5}$ alloys seems to be related to this.

IV. CONCLUSIONS

We have performed first-principles total-energy pseudopotential calculations for the $(\mathrm{InAs})_1/(\mathrm{GaAs})_1$ monolayer superlattice in the (001) orientation, and predicted that bulk $(\mathrm{InAs})_1/(\mathrm{GaAs})_1$ is thermodynamically unstable towards disproportionation into zinc-blende constituents. We have estimated the microscopic strain and the chemical contributions to the superlattice formation energy, and concluded that this instability is attributed to the unfavorable charge transfer from the GaAs layers to the InAs layers. The ordered $(\mathrm{InAs})_1/(\mathrm{GaAs})_1$ structure, once constructed, will persist metastably because of large activation barriers and exceedingly low-diffusion coefficients at laboratory temperatures. We have found that epitaxial $(\mathrm{InAs})_1/(\mathrm{GaAs})_1$ grown on InAs, InP, or GaAs substrates is much less unstable than bulk $(\mathrm{InAs})_1/(\mathrm{GaAs})_1$ since the microscopic strain contribution becomes negative under epitaxial-growth conditions. This is because the epitaxial-induced strain is accommodated more successfully in $(\mathrm{InAs})_1/(\mathrm{GaAs})_1$ than in InAs and GaAs. By using the concept of the midgap point and employing a tight-binding scheme, we have presented a simple criterion for the charge transfer in monolayer superlattices. The criterion is confirmed by the direction of charge transfer determined from the first-principles calculations for $(\mathrm{InAs})_1/(\mathrm{GaAs})_1$, $(\mathrm{InP})_1/(\mathrm{GaP})_1$, and $(\mathrm{GaAs})_1/(\mathrm{AlAs})_1$. It is predicted that $(A^{\mathrm{III}}B^{\mathrm{V}})_1/(A^{\mathrm{III}}C^{\mathrm{V}})_1$ monolayer superlattices may be thermodynamically stable in epitaxial forms.

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