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Thermodynamic Instability of Ultrathin Semiconductor Superlattices: The (001) (GaAs)$_1$(AlAs)$_1$ Structure

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First-principles total-energy pseudopotential and all-electron calculations predict (001) (GaAs)$_1$-(AlAs)$_1$ and (CdTe)$_1$(HgTe)$_1$ superlattices to be intrinsically unstable towards disproportionation into compounds. This instability is traced to unfavorable charge redistribution in the system.

Many disordered[1] or artificially ordered[2] semiconductor systems are manifestly *metastable* in temperature and composition ranges in which they are usually characterized and utilized. Such are disordered $GaAs_xSb_{1-x}$ alloys[1] (grown in the range of thermodynamic immiscibility of GaAs and GaSb), and *ordered* $(A^{III}B^V)_{1-x}$-$(C_2^{IV})_x$ alloys[2] (judged by their equilibrium phase diagrams to spinodally decompose). Metastable systems come to exist through *kinetic* rather than thermodynamic control, e.g., by nonequilibrium growth techniques.[1,2] They owe their thermal stability[1,2] to large reorientation activation barriers,[2] small thermodynamic driving forces,[1,2] and exceedingly low diffusion coefficients at laboratory temperatures.[1,2]

Despite extensive study, it is as yet unclear whether artificial semiconductor superlattices $(AC)_m(BC)_n$ are thermodynamically (intrinsically) stable or metastable. Current understanding can be characterized as follows. *Disordered* (D) isovalent alloys $A_xB_{1-x}C$ are *known* to have positive enthalpies of mixing[3] $\Delta H^D(x)$, so that at a sufficiently low temperature T_c the negative entropy term $-T_c\Delta S^D$ is overwhelmed by the positive ΔH^D, leading eventually[3,4] to disproportionation. Most contemporary theoretical models[3,4] analyze this instability of $A_xB_{1-x}C$ *alloys* via models that do not distinguish them from *ordered compounds* $A_mB_nC_{m+n}$ of the same composition. Such are, e.g., elastic models[4] which attribute $\Delta H > 0$ to the destabilizing role of microscopic strain associated with a mismatch Δa between lattice constants of AC and BC. Since thin superlattices $(AC)_m(BC)_n$ are most naturally regarded as ordered compounds[5]—e.g., an $m = n = 1$ superlattice in the (001) orientation is crystallographically identical to an ABC_2 compound with the simple tegragonal $p\bar{4}m2$ space group[5,6] (having a CuAu-I-like A-B sublattice)—these models would judge both alloys and superlattices (having nearly the same Δa) intrinsically unstable at low temperatures. However, Srivastava, Martins, and Zunger[6] demonstrated that $\Delta H^D > 0$ does not require *ordered* (O) phases to be unstable too because (i) a *chemical* energy term, neglected by other models,[4] may render ΔH^O

negative, and (ii) *coherently ordered* arrangements of bonds can reduce strain imposed by bond-length mismatch better than do *disordered* arrangements.

Perhaps the best-studied superlattice— $(GaAs)_m$-$(AlAs)_n$—exhibits,[7-9] however, a delicate energy balance: It has a nearly vanishing $\Delta a = R_{AlAs} - R_{GaAs}$ $= 0.0009$ Å at growth temperatures ~ 800 K and consequently a nearly vanishing[3] ΔH^D (hence, ordering offers but a small reduction in strain), yet Al differs (slightly) from Ga in electronegativity (hence, charge transfer may stabilize the system). This delicacy is highlighted by the disparate views on stability of the $(GaAs)_1(AlAs)_1$ superlattice. Kuan *et al.*,[7] having observed ordered GaAlAs$_2$ even in spontaneous growth, characterized it as the thermodynamic equilibrium state of $Ga_xAl_{1-x}As$, as did Petroff[8] for the layer-by-layer–grown superlattice. On the other hand, Phillips[10] suggested that this phase was intrinsically unstable but stabilized via pinning by oxygen impurities, and Ourmazd and Bean[11] suggested that it was stable only because of extrinsic substrate strain effects. Theoretical estimates for the formation enthalpy of the ordered (O) superlattice similarly range (referring all energies to a primitive cell of four atoms) between stability ($\Delta H^O = -1.5$ meV, obtained from empirical tight binding,[12] or $\Delta H^O = -20$ meV, from a cluster calculation after optimization of bond lengths[13]) and instability ($\Delta H^O = +9.2$ meV in a recent calculation using relativistic pseudopotentials[14]).

We here apply first-principles pseudopotential and all-electron total-energy methods to study stability of (001) $(GaAs)_1(AlAs)_1$ and $(CdTe)_1(HgTe)_1$ superlattices. We clarify the physical factors which control this instability and trends with superlattice thickness.

Zinc-blende AC and BC compounds we take to have cubic lattice constants a_{AC} and a_{BC}, respectively; their (001) $(AC)_1(BC)_1$ superlattice (inset of Fig. 1) is characterized by two lattice parameters a and c (where $\eta \equiv c/a$ denotes the tetragonal ratio) and the C-atom displacement parameter $u \equiv \frac{1}{4} + (R_{AC}^2 - R_{BC}^2)/\eta^2a^2$. For $\eta = 1$ and $u = \frac{1}{4}$, one has $R_{AC} = R_{BC} = \sqrt{3}a/4$, as in the cubic zinc-blende structure. The enthalpy of formation
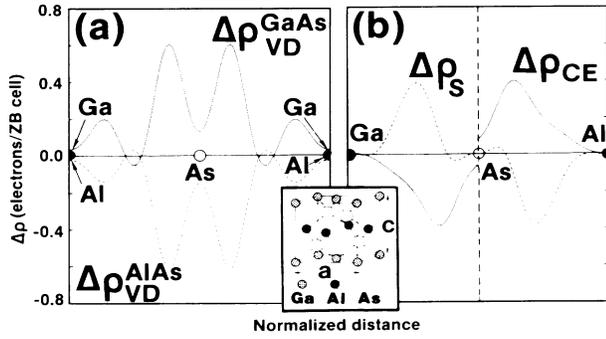
FIG. 1. Redistribution of valence charge density associated with (a) dilation (compression) of zinc-blende (ZB) GaAs (AlAs) to equilibrium lattice constant of GaAlAs$_2$ and with (b) formation of unrelaxed superlattice at a_{eq} ($\Delta\rho_{CE}$) and relaxation of structural parameters c and u ($\Delta\rho_s$). Vertical dashed line [in (b)] indicates interface through As atom. Inset: The (GaAs)$_1$(AlAs)$_1$(001) superlattice unit cell.

TABLE I. Calculated pseudopotential (PS), all-electron LAPW, and experimental (experiment, Ref. 19) lattice parameters a (0 K, extrapolated), bulk moduli (B), and cohesive energies E_c (eV/atom) for zinc-blende GaAs and AlAs. Calculated LAPW lattice parameters for CdTe and HgTe are respectively 6.473 and 6.492 Å (observed values are 6.481 and 6.461 Å).

| | GaAs | | | AlAs | | |
	a (Å)	B (GPa)	E_c	a (Å)	B (GPa)	E_c
PS	5.518	78.0	4.14	5.604	73.4	4.39
LAPW	5.690	76.2	3.88	5.661	76.1	4.33
Expt.	5.642	75.4	3.35	5.652	∼77	3.80

of ordered *bulk* ABC_2 is its equilibrium (eq) energy relative to its constituents, also at equilibrium,

$$\Delta H^O = E_{ABC_2}(a_{eq}, u_{eq}, \eta_{eq}) - E_{AC}(a_{AC}) - E_{BC}(a_{BC}).$$

(1)

We have calculated ΔH^O for (GaAs)$_1$(AlAs)$_1$ using the first-principles self-consistent pseudopotential total-energy method[15] within the local-density formalism. We use analytically continued[16] semirelativistic nonlocal pseudopotentials and a plane-wave basis with a fixed kinetic-energy cutoff of 16 Ry (corresponding to about 310 basis functions for AC and BC, and 620 basis functions for ABC_2). The Ceperley-Alder exchange-correlation functional parametrized by Perdew and Zunger[17] was used and the two **k** points obtained by folding of the two Chadi-Cohen face-centered–cubic special **k** points[18] into the smaller superlattice Brillouin zone have been used, guaranteeing total energies of identical precision for the superlattice and its zinc-blende constituents. (Convergence tests indicate a precision better than 0.2 meV per four atoms with respect to self-consistency. The excess energy changes by less than 0.6 meV per four atoms when sampling is increased from two to twelve special **k** points.) Calculated and experimental[19] ground-state properties of GaAs, AlAs, CdTe, and HgTe are summarized in Table I; pseudopotential results are similar to those published previously[20] using this method. Our (and others'[20]) predicted pseudopo-

tential bond-length mismatch $R_{AlAs} - R_{GaAs} = 0.087$ Å greatly exceeds the observed value (0.010 Å at 0 K).

We examine ΔH^O under three distinct structural conditions. First, given the small experimental bond mismatch (Table I), we neglect structural distortions ($u \neq \frac{1}{4}$, $\eta \neq 1$) and take a_{eq} for GaAlAs$_2$ to be the average of theoretical GaAs and AlAs. Using the pseudopotential method we find $\Delta H^O = +25.0$ meV. Though the precision of the calculation is high, some uncertainty regarding use of a pseudopotential approximation may exist, and so we checked these results using the all-electron linear augmented-plane-wave (LAPW) method,[21] finding at the average *experimental* lattice constant $\Delta H^O = +25$ meV, in excellent agreement with the pseudopotential result given the radically different natures of the two computational schemes.

We next calculate E_{ABC_2} of Eq. (1) at the *relaxed* (a, u, η) values. We use Keating's[22] valence-force-field (VFF) model to find the relaxed geometry for use in self-consistent total-energy calculations. We find in the pseudopotential model $\Delta H^O = +21.3$ meV at $(a, \eta, u) = (5.560$ Å, 1.000, 0.246), and in the all-electron LAPW model $\Delta H^O = +19$ meV at (5.676 Å, 1.000, 0.252), indicating a rather small ∼5-meV stabilization due to relaxation. This should be compared to the *attractive* $\Delta H^O = -50$ meV obtained recently[23] for CdMnTe$_2$ (relative to ferromagnetic MnTe), to $\Delta H^O = -330$ meV/atom for[24] SiC, and to the small repulsive $\Delta H^O = +12$ meV we obtain here, using the LAPW method for CdHgTe$_2$ in the CuAu-I structure, where $u_{eq} = 0.252$.

One may wonder if *epitaxial* (rather than *bulk*) growth alters our conclusions. For *epitaxial* growth in a dislocation-free fashion on a substrate (s) with lattice parameter a_s perpendicular to the growth direction, the effective enthalpy of formation of Eq. (1) becomes instead[24]

$$\delta H(a_s) = E_{ABC_2}(a_\| = a_s) - E_{AC}(a_\| = a_s) - E_{BC}(a_\| = a_s).$$

(2)

Parallel (∥) to the substrate the lattice parameters of ABC_2, AC, and BC are constrained to equal a_s; all other structural degrees of freedom adjust to minimize the system's energy. For $\Delta E_{ss}(a_s) \equiv \delta H(a_s) - \Delta H^O < 0$ the epitaxial system is stabler (or less unstable) than the bulk-grown system. Using the pseudopotential method for a substrate lattice con-

stant $a_s = a_{GaAs}$ we find that AlAs dilates tetragonally to $\eta_{AlAs} = 1.030$ but GaAlAs$_2$ distorts only to $\eta = 1.015$, leading to $\delta H(a_{GaAs}) = +14.5$ meV. For AlAs as substrate we find $\eta_{GaAs} = 0.969$ and GaAlAs$_2$ distorts only to $\eta = 0.985$ with $\delta H(a_{AlAs}) = +16.0$ meV. We hence find that ΔE_{ss} (-6.9 and -5.4 meV for GaAs and AlAs, respectively, as substrates[25]) is insufficient to render the epitaxial formation enthalpy δH negative. We hence conclude that the superlattice is *thermodynamically un-*

stable in either bulk ($\Delta H^O > 0$) or epitaxial ($\delta H > 0$) forms.

Using pseudopotential results we now analyze the physical mechanisms behind this instability ($\Delta H^O = 21.3$ meV) by describing formation of ABC_2 as a stepwise process,[6] permitting decomposition of ΔH^O of Eq. (1) into physically recognizable terms. *First,* compress or dilate the constituents AC and BC to the equilibrium lattice constant a of ABC_2, investing a volume deformation (VD) energy

$$\Delta E_{VD} = [E_{AC}(a) - E_{AC}(a_{AC})] + [E_{BC}(a) - E_{BC}(a_{BC})]. \tag{3}$$

Since deformation of equilibrium structures in involved, $\Delta E_{VD} > 0$; self-consistent calculations yield $\Delta E_{VD} = +14.2$ meV. The change in charge density, $\Delta\rho_{VD}(r)$, associated with VD [Fig. 1(a)] corresponds to a reduction (increase) of charge on Ga—As (Al—As) bonds. *Second,* bring the "prepared" AC and BC units together to form ABC_2, without relaxing the bonds, with an energy change

$$\Delta E_{CE} = E_{ABC_2}(a, u = \tfrac{1}{4}, \eta = 1) - E_{AC}(a) - E_{BC}(a) \tag{4}$$

due to possible charge exchange (CE) between atoms. Electron charge flows [$\Delta\rho_{CE}(r)$, Fig. 1(b)] from the Ga—As bond to the Al—As bond (in the direction of increased electronegativity on Phillips's scale). The associated energy can be modeled electrostatically, permitting the cation charge difference $\Delta Q = Q_A - Q_B$ in ABC_2 to differ from that ($\Delta q = q_A - q_B$) in the isolated AC and BC compounds, giving an excess Madelung energy of the ternary over the binary constituents (in electron volts per four atoms with R in angstroms)

$$\Delta E_{CE} \approx 14.40(\Delta q^2/R)[\tfrac{1}{2}\alpha^{ZB} - \tfrac{1}{16}\sqrt{6}\alpha^{(1,1)}(\Delta Q/\Delta q)^2], \tag{5}$$

where $\alpha^{ZB} = 1.638\,055$ and $\alpha^{(1,1)} = 1.594\,367$ are Madelung constants and $R = \sqrt{3}a/4$ is the bond length. Formation of the superlattice must *amplify* the relative cation charge disparity $\Delta Q/\Delta q$ by ~ 1.83 to make ΔE_{CE} negative, a condition not met [Fig. 1(b)] for atoms as similar as Ga and Al. (Using LAPW we find within the atomic spheres $\Delta q = 0.074e$, $\Delta Q = 0.06e$; hence ΔE_{CE} accounts for most of ΔH^O within the model.) Direct pseudopotential calculations give $\Delta E_{CE} = +10.7$ meV. *Finally,* a structural (S) energy is involved in relaxing the geometry of ABC_2, i.e.,

$$\Delta E_S = E_{ABC_2}(a_{eq}, u_{eq}, \eta_{eq}) - E_{ABC_2}(a_{eq}, u = \tfrac{1}{4}, \eta = 1). \tag{6}$$

This step involves two contributions: release of elastic strain energy ΔE_{VFF} of ABC_2 upon relaxing of its bond lengths and angles, and a polarization (Pol) contribution $\Delta E_{Pol} \equiv \Delta E_S - \Delta E_{VFF}$ associated with relaxation-induced charge transfer $\Delta\rho_S(r)$ [Fig. 1(b)]. For GaAlAs$_2$ we find $\Delta E_{VFF} = -7.8$ meV since the superlattice is better able to accommodate strain than equivalent amounts of its constituents at the same lattice parameter, and a *positive* $\Delta E_{Pol} = +4.2$ meV. The net charge rearrangement is from the *stronger* AlAs bond (see E_c in Table I) to the *weaker* GaAs bond, exactly the opposite from what was found in SiC[24] and CdMnTe$_2$,[23] which are stable.

The total formation enthalpy of Eq. (1), the sum of Eqs. (3), (4), and (6), can be written $\Delta H^O = (\Delta E_{VD} + \Delta E_{VFF}) + (\Delta E_{CE} + \Delta E_{Pol}) \equiv \Delta E_{ms} + \Delta E_{chem}$. The first

term in parentheses represents the total microscopic strain (ms) energy, the second the total chemical (chem) energy. Since the CuAu-I structure lacks sufficient degrees of freedom to yield zero strain,[24] we have $\Delta E_{ms} = +6.4$ meV > 0. Evidently, the superlattice is stable only if ΔE_{chem} is negative and overwhelms ΔE_{ms}. For GaAlAs$_2$ we found $\Delta E_{chem} = +14.9$ meV, similar to the chemical energy 0.4 kcal/mole $= +17.3$ meV measured for a disordered Ga$_x$Al$_{1-x}$As alloy at $x = \tfrac{1}{2}$ by diffuse x-ray scattering.[26] Even simulating the small experimental lattice mismatch Δa by setting $\Delta E_{ms} \simeq 0$, we still predict[27] $\Delta H^O > 0$. Since, however, in systems with a finite Δa the disordered phase has a higher strain energy than corresponding ordered structures,[6] once formed, the ordered compound will persist metastably since kinetic activation barriers for disordering and decomposition are insurmountable at low temperatures.

Having identified the chemical energy as the major source of instability in the system, we generalize the simple model of Eq. (5) to a longer-period $(AC)_m(BC)_m$ superlattice. Assuming charge transfer between interfacial A-B atoms only (others retaining charges q_A and q_B of the binary systems, with the C atom charge preserving local charge neutrality) yields for large m per four atoms an excess energy $\Delta E^m \simeq 2\sigma/m$ where the "interface energy" is $\sigma = (\Delta q^2/4R) \times \{a - b[(\Delta Q/\Delta q) + c]^2\}$ and a, b, and c are positive constants of order 1. For sufficiently small $\Delta Q/\Delta q$ (as found above for $m = 1$) $\sigma > 0$; only for $\Delta Q/\Delta q \geq 1.25$ is the interface attractive ($\sigma < 0$). Note

that for $\sigma > 0$ an m superlattice is *less unstable per bond* than an $m-1$ one, since $\Delta E^m \sim + |\sigma|/m$. Hence, provided disproportionation is inhibited (e.g., by large activation barriers), *an unstable thin superlattice has an energy incentive to grow.* Conversely, for attractive ($\sigma < 0$) interfaces, a thin superlattice has no thermodynamic incentive to grow.

The driving force for ordering of GaAlAs$_2$ observed[7] at ~ 970 K remains unclear. Possibly a *surface*-controlled mechanism is at work: Deposition of Al on the GaAs(110) surface above ~ 800 K produces a segregation effect[28] whereby the Al is exchanged with the surface Ga to produce an AlAs layer on top of GaAs. Such fluctuating segregation sequences may produce long-range order.

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