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Stability and electronic structure of ultrathin [001](GaAs) (AlAs) superlattices

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The general issues of stability towards disproportionation or disordering of (AC) (BC) super-
lattices are addressed by simple model calculations based on detailed first-principles results for the (GaAs), (AlAs), [001]-orientation alternate-monolayer superlattice. Valence-force-Seld (VFF) cal-culations permit isolation of strain-related contributions to the superlattice formation energy and a simple electrostatic energy model highlights the importance of charge transfer in stabihzing or destabilizing such ordered phases. We predict that bulk {GaAs)&(A1As)& is in fact unstable with respect to disproportionation into zinc-blende constituents because of insu5cient Ga-Al charge
transfer. Epitaxial growth on GaAs or AlAs simply makes this structure less unstable. A simple
semiquantitative model for [001] (AC},(BC), extracted from detailed self-consistent calculations makes clear the competition between (destabilizing) strain effects and {potentially stabilizing) charge transfer effects. %e extract trends for thicker superlattices with the aid of VFF calcula-tions and generalizations of the electrostatic model. %e find that unstable thin superlattices be-come (per bond) less unstable as the repeat period increases, while stable ones become less stable per bond. Kinetic factors or surface effects must be invoked to explain the spontaneous oc-currence of (GaAs) (AlAs) structures. The electronic structure of (GaAs)l(AlAs)l is analyzed in
detail and interpreted in terms of simple distortions and band folding of the virtual-crystal-
approximation band structure.

I. INTRQDUCTION

Recent perfection' of atomic-scale control over nu-cleation and growth using modern crystal-growth tech-niques such as molecular-beam and liquid-phase epitaxy and

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al) entropy between the ordered phase and the binary
constituents, awhile the disordered alloy has a free energy
of formation

bG (x, T)=AH (x)—TM (x), (4)
where ES (x}includes electronic and vibrational as well
as con6gurational' contributions. In what follows we will examine the stability of perfectly ordered superlat-tices, using

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Al

ever, of distortions of bond angles from the ideal
tetrahedral value 109.5. Conversely, one could achieve
ideal bond angles at the expense of bond-length distor-
tions. Unlike for zine-blende or CuPt binary structures,
it is impossible' in the lattice-mismatched (AC),(BC), superlattice of Fig. 1(a) to simultaneously preserve "ideal" d ~c and d~& bond lengths and perfect tetrahedral bond angles. The equilibrium

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TABLE I. Nonrelativistic (NR) and semirelativistic tSR)
all-electron atomic orbital eigenvalues s„c~(eU) and orbital ra-

dii (r„,},and (r„r} (a.u.) for Ga, Al, and As using the local-
density approach with Ceperley-Alder (Ref. 43) exchange-
correlation potentials.

—8.93 —9.17

Ga
2.37
2.33

—2.77 —2.74

3.37
3.37

—7.81 —7.84

Al
2.55
2.53

—2.80 —2.79

3.44
3.44

As
1.97
1.93

—5.38 —5.35

2.55
2.55

the local-density-functional formalism and the Ceperley-
Alder exchange-correlation functional as parametrized

by Perdew and Zunger. The proximity (-15 eV) of
the Ga 4s

as

the

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TABLE III.

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dered superlattice, increasing its entropy bS

. Each
effect reduces the entropy change AS

—AS upon dis-
ordering, reducing the calculated Q.
We conclude from the pseudopotential calculations described above that the energetic hierarchy for the (GaAs),

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Energies

We have calculated the terms of Eq. (15) as follows:
bE„&, bECE, and EEs were each obtained directly from the defining equations [Eqs. (11)-(13)] using

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0.8
I
I
I
I

I
I

I

g Q4-
Cl

QQ Ga

Q

O

CL

C3 -04-

I
I

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I

I

I
I
I
I
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I

-0. I 8

"..—."&pvo
- —- - — kp go +hpCE

I
I
I
I
I
I

E

I

+hp =kp

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AI

I

I
I

i

I

I

I
4

I
I

I
t
I
I
t

Normalized Oiatance

FIG. 4. Net charge density redistribution (with respect to equilibrium binary compounds) along bonds after volume de-formation (VD, dotted line), charge exchange (VD + CE, dashed line), and net (VD + CE+- S, solid line).

Batra et al., which found an opposite charge transfer, with Pickett et al. using empirical pseudopotentials [who

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(a),:

20-

Cl 1
N

16- (
0

C I

la 12.

Q. 6

RL
non-Zs '

p1.0
0.8

0.6

" 02
N

a /

-OA

-0.6

-0.8

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terms" for the disordered phase (see Appendix B). They
erroneously predicted

a substantial stabiIization of

4EM~,~„„+4E~sover AEMd, &„„&+AEos.Using their values for GaAs/AIAs, i.e.

, Uc

=9.49 eV,
EQ /2

=0.02e, and the experimental average GaAs/AlAs bond length [but with the corrected expres-
sion, or Eq. (25)] shows the random alloy to have an
energy comparable (within

a fraction of

a meV} to that
of the ordered superlattice, including both Madelung and an-site terms. Since the formation energy

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2.4—

r,

'R4

,

X3

— -=- r)
L)

VCA

Qao qAIO SAs (GaAI)&(AIAs)&

(b) (c)

AlAs

(a)

FIG. 8. Conduction-band eigenvalues at I, L, and X points of the face-centered-cubic Brillouin zone at a =5.56 A for GaAs, A1As, 6ctitious Ga05Alo 5As VCA alloy, and unrelaxed {GaAs)&(A1As),.

effects: (a} deformation potential-induced shifts in the constituents as GaAs (AlAs) is dilated

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.';-0.15 -;:::;:-.
-0.03--

not p character, and exhibits the usual antibonding s character; its splitting samples only the difFerence in Ga and Al I =0 pseudopotentials. The next-highest energy VCA state L, &, has both cation s and p character. In-terestingly, the superlattice compatibility relations re-quire this state to split into an Rl, state [consisting of Ga s and p, orbitals and Al (p„+p~) orbitals] and a
complementary R4, state. This is evident in Figs.

10(g)—10(i); the splitting ~ e(R~)—e(R „)~

is the largest
of all conduction bands sho~n because it samples the difFerence in both the s- and p-wave pseudopotentials for Ga and Al. One result of this ampli6cation of cation difference is that (GaAs)I(AIAS), is indirect by way of the

R (L„)point (whereas the VCA alloy is indirect via X„).Finally, the VCA X&, state, with strong cation s character, is split [Figs. 10(j)-10(1)]into states M„and M2, with cation-centered lobes.
The preceding discussion shows that the states of or-dered GaAJAsz difFer from those of the disordered Gao&A105As alloy. This can be quantized by de6ning "optical bowing parameters" for the ordered (ord) phase
GaAlAs2 as

-0.7S
-0.5

.

:; -0.25

b„d(I„)=4[a(I„)—e(I"„(I'I,))],

b,„d(X„) =4[a(X1,)—S(MS,(XI,))],

b„d(L„)=4[K(L„)—

„3P5t/Xi13 9350.01

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{GaAa)& (AIAI)& {

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m —1 layers of As atoms each coordinated by four Ga
atoms and m —1 coordinated by four Al atoms, and two
interfacial layers of As atoms coordinated by two Ga and two Al atoms. Since such layers are characteristic,
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respectively, of (epitaxially-constrained) GaAs, A1As,
and (GaAs), (A1As),, we may write (to the extent that a
given layer is coupled only to its neighboring layers) per
four atoms

EMs[(GaAs) (A1As), a)]= IEMs[GaAs, a]+EMs[A1As, a]I+—EMs[(GaAs), (A1As)i, a], (34)

where all energies on the right-hand side are per cation-
anion pair. This model would predict, using the VFF re-
sults for tetragonally-distorted GaAs and A1As and
(GaAs), (A1As), at a, that

EM~&[(GaAs) (AIAs), a)]=4.320—0.279/m

(in meV per four atoms); a least-squares fit of the form a +h /m directly to the VFF results for m =1,2, 3 yields EvMs" —4.318—0.276/m. Thus an extremely simple
model accounts very well for actual VFF calculations.
Identical calculations (in which we take each binary to
be at its equilibrium lattice constant, ignoring the small
b,a for real GaAs/A1As) may be made for the micro-
scopic strain (MS} contribution to the formation energy
of (GaAs) (AlAs), yielding (per four atoms)

b,EMs lm =AEoMs[(GaAs), (AIAs),]/m =2o /m,

(35}

where we have identi6ed the interfacial energy o, using the fact that the (1,1) superlattice primitive cell consists entirely of two interfaces.

8. Electrostatic Madelung energy model

The VFF results above, together with the first-principles results ' ' '

strongly support a picture in
which only the regions near the interfaces in the (AC) (BC) superlattice differ from their bulk counter-

parts. Taking, therefore, Q„=q„andQs+qs only for
interfacial sites, we find for large m that

b EM,d„„„s(m, m) can be written (per four atoms) as

b E,M)d„„s/m=(bq) /mR [A —B(bQ/hq+C)]

with R an AC or BC bond length and A =2.034,
8 =0.7722, and C=0.3694. This expression predicts that, for large m, b,Q/bq must exceed 1.54 for the (m, m) superlattice to be stable. This may be written in the form (per four atoms) bE&E[(AC) (BC)]=2o /m; for b,Q/hq =1 it predicts o =0.293(hq) /R, while Eq.
(23) for m =1 yields o =0.287(b.q) /R, corroborating the scaling form hE (m, m)=EE (1,1)/m of Eq. (35).

C. Stability and growth of thicker superlattices

Having found the form bH (m, m) =2cr/m
=b,H (1,1)/m per bond to emerge from two extremely different model calculations for superlattice stability-one emphasizing strain eff'ects (and yielding b,EMs) and the other Madelung charge transfer effects (and yielding approximately EEcE)—we next examine its implications

for superlattice growth. For o «0 the A -C-8 interface is stable with respect to —, '[A-C-A+B-C-B]. Since hH (m, m) per bond scales as 1/m, however, in thermo-dynamic equilibrium if o &0 there is no energy incentive for a thin superlattice to grow thicker because the thicker system is less stable per bond. On the other hand [as we

found above for [001] (GaAs), (A1As),],if o ~0 a thin su perlattice mill grour thicker since a thick superlattice is less unstable per bond than a thin one. It

because

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GaSb), and ordered (III-V), „(IV&)„alloys (although judged by their equilibrium phase

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quite poor, particularly for small clusters. The smallest
cluster size that is reasonably configuration independent
has not yet been determined.

" %e note that the ex-
tremely close agreement between the effective Madelung
constant for

a disordered alloy obtained via

a

superposition-of-clusters approach and their truncation of the Madelung energy [Eqs. (83) and (84)] shows that this speculation is incorrect.
Analogous superposition procedures may be carried out for on-site Coulomb contributions for the disordered alloy (and give results identical to those of van Schilf-gaarde

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=
+ 29.

3

+ 78.

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