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0.4

Ga

- Al

dp

' ' I', b',)

Ga
~~ Ga

As

'-' Al~

.&PcE

- AI

TA BLE I. Calculated pseudopotential (PS), all-electron
LAPW, and experimental (experiment, Ref. 19) lattice param-eters a (0 K, extrapolated), bulk moduli (8), and cohesive en-ergies E, (eV/atom) for zinc-blende GaAs and AlAs. Calcu-lated LAPW lattice parameters for CdTe and HgTe are re-spectively 6.473 and 6.492 A (observed values are 6.481 and 6.461 A).

gp

AIAS
-0.8

e+&oC
Q~~ '

a
0 ~
Ga Al As
Normalized distance

FIG. 1. Redistribution of valence charge density associated
with (a) dilation (compression) of zinc-blende (ZB) GaAs
(AlAs) to equilibrium lattice constant of GaAIAsz and with (b) formation of unrelaxed superlattice at a,q

(ApcE) and re-
laxation of structural parameters c and u (Ap,). Vertical
dashed line [in (b)] indicates interface through As atom. In-
set: The (GaAs) ~ (AlAs) ~(001) superlattice unit cell.

We have calculated AH for (GaAs)~(A1As)t using
the first-principles self-consistent pseudopotential total-energy method ' within the local-density formalism. We
use analytically continued '

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 func-
tions for ABC2). The Ceperley-Alder exchange-
correlation functional

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stant a, =aG,&, we find that AlAs dilates tetragonally to
g~~~, =1.030 but GaAlAs2 distorts only to g =1.015,
leading to hH(ac„A,) =+14.5 meV. For A1As as sub-
strate we find gG,~, =0.969 and GaAlAs2 distorts only to
r1=0.985 with SH(a~~p„) =+16.0 meV. We hence find
that AE„(—6.9 and —5.4 meV for GaAs and A1As, re-
spectively, as substrates) is insufficient to render the
epitaxial formation enthalpy 8H negative. We hence
conclude that the superlattice is thermodynamically un-

stable in either bulk (hH &0) or epitaxial (crH &())
forms.
Using pseudopotential results we now analyze the

physical mechanisms behind this instability (hH =21.3 meV) by describing formation of ABC2 as a stepwise
process, permitting decomposition of hH of Eq. (1)
into physically recognizable terms. First, compress or
dilate the constituents AC and BC to the equilibrium lat-
tice constant a of ABC2, investing a volume deformation
(VD) energy

&EVD = [E~c(a)—E~c(a~c)]+[E'ac(a) EBc—(aBc)] (3)

Since deformation of equilibrium structures in involved, BEAD & 0; self-consistent calculations yield BEAD =+14.2
meV. The change in charge density, dpvo(r), associated with VD [Fig. 1(a)] corresponds to a reduction (increase) of
charge on Ga—As (Al—As) bonds. Secondbri, n g the "prepared" AC and BC units together to form ABC2, without relaxing the bonds, with an energy change

tsEcE =Epic, (a, u = —,

, rl =1)—Egc(a) —E~c(a) (4)

due to possible charge exchange (CE) between atoms. Electron charge flows [ApcE(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 dilference Ag =Q~ —Qtr in ABC2 to difler from that
(Aq =qz —qtr) 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)

14.40(tt q

2/R) [

azB J6a '

(gg/Aq)],

where a =1.638 055 and a

"

=1.594 367 are
Madelung constants and R =J3a/4 is the bond length.
Formation of the superlattice must amplify the relative
cation charge disparity hg/Aq by —1.83 to make AEcE
negative, a condition not met [Fig. 1(b)l for atoms as
similar as Ga and Al. (Using LAPW we find within the

atomic spheres Aq =0.074e, Ag =0.06e; hence hEcE ac-
counts for most of /s. H within the model.) Direct pseu-
dopotential calculations give AEc~=+10.7 meV. Fi-
nallyastructu, ral (S) energy is involved in relaxing the
geometry of ABC2, i.e.,

~Es EABcr(aeq~ tteqi rleq) EABc2(aeq~ tt 4

(6)

This step involves two contributions: release of elastic
strain energy AEvFp of ABC2 upon relaxing of its bond
lengths and angles, and a polarization (Pol) contribution
AEpo~ —=AEg AEvFF associated with relaxation-induced charge transfer Aps(r) [Fig. 1(b)]. For GaA1As2 we find hEvpF= —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 pos-

itii e AEp, ~ =+4.2 meV. The net charge rearrangement
is from the stronger A1As bond (see E, in Table I) to the weaker GaAs bond, exactly the opposite from what was
found in SiC and CdMn Te2, which are stable.
The total formation enthalpy of Eq. (1), the sum of
Eqs. (3), (4), and (6), can be written hH =(AEvD +AEVFF) + (lsEcF +&Ep,)) =&E,+&E,h,~. The first—

(5)

term in parentheses represents the total microscopic
strain (ms) energy, the second the total chemical (chem)
energy. Since the CuAu-I structure lacks sufficient de-
grees of freedom to yield zero strain, " we have
8E,= +6.4 meV & 0. Evidently, the superlattice is
stable only if hE, h, is negative and overwhelms hE For GaAlAs2 we found hE, h, =+14.9 meV, similar to
the chemical energy 0.4 kcal/mole =+17.3 meV mea-
sured for a disordered

for

—4 Td (negatmetae)Tj y

9

t1 Td (the)Tficirs

relaxm

d (of)Tj ET BT /Xi2 9.26 Tf 313.78 Td (ed (superj ET BT /Xi2 11.4 Tf 378.67 328.51.82 (2(ch.)Tj ET BT /Xi2 8.79 Tf 2378560187 Td (d (of)Tj ET BT /Xi2 8.77 Tf 451.11 3

oTj EET BT /Xi2 8.21 Tf 194.64 488.39 55 (the)Tre-tj E ETe BT /Xi2 8.94 Tf 476.33 395 T9 55 (charge)Tj EET BT /Xi2 8.84 Tf 54.4449909.2d6Td (the)T ET contri tota

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that for cr) 0 an m superlattice is less unstable per bond

than an m —I one, since hE —+ i cri/m. Hence, pro-
vided disproportionation is inhibited (e.g., by large ac-
tivation barriers), an unstable thin superlattice has an
energ J i ncenti ve to gro~. Conversely, for attractive
(cr &0) interfaces, a thin superlattice has no thermo-dynamic incentive to grow.
The driving force f'or ordering of GaAlAs2 observed
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 segre-gation eAect whereby the Al is exchanged with the sur-face Ga to produce an AlAs layer on top of GaAs. Such
fluctuating segregation sequences may produce long-
range order.

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