PHYSICAL REVIEW B VOLUME 44, NUMBER 20 15 NOVEMBER 1991-II Spontaneous surface-induced long-range order in Gao 5Ino 5P alloys James E. Bernard, S. Froyen, and Alex

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Chalcopyrite CuAu- i CuPt

OA

QB
C

FIG. 1. Some of the observed ordered 3D structures of
adamantine pseudobinary ABC2 semiconductors.

dering of the random alloy: for certain strain-minimizing
ordered structures 0 one can have AHbulk ~Hbulk (0) (D)
gardless of the sign of the two individual formation
enthalpies. The sum of the volume-deformation and strain-relief energies (total strain) can be zero only in to-
pologically unconstrained" binary structures (e.g., zinc
blende and RH1), which possess sufficient structural de-grees of freedom to accommodate all of the bonding con-
straints. All pseudobinary adamantine structures are
constrained, so for h a %0 their total strain energy is posi-tive. '
(iii) The charge excha-nge energy reflects chemical in-
teractions attendant, e.g.

to

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A1InP2/GaAs (100), GalnAs~/InP (100) and
GaInAsP, 3

InA1As2/InP (100), Ga2AsP on a (100) al-
loy substrate and A1GaInP/GaAs (100).
Rhombohedral-type ordering was seen in Si, Ge„.
The prototype examples for ordering in pseudobinary
B C alloys that we wish to discuss here are the CP
ordering of GaInP2/GaAs (100) and the CA ordering of
AIGaAsz/GaAs (110). Our foregoing discussion on the
stability of various bulk intersemiconductor phases serves to explain why these particular forms of spontaneous long-range order are especially interesting.
(i) These isovalent alloys are known '

to have positive
mixing enthalpies AHb„&I, &0 when disordered, so or-
dered phases can represent stable equilibrium only in the
unusual case where special structures 0 have EHb„&k &0
despite AHb„&'& & 0. Initially, a nu~ber of calculations on
A1GaAs2 indicated that AHb„&&' &0 for the observed
CA structure. However, these were later shown to
be either incomplete or incorrect, so that in fact

hH' ')0 (actually, even' b,H' ') b,H' '

is true).
Calculations on GaInP2 also show' that

EHb„&&' & AHb„&'k &0. Hence, the observed ordering can-not represent bulk equilibrium.
(ii) Even if phase separation were slowed down by bulk kinetic limitations, calculations of AHb„&k and our forego-
ing discussions show that the next lowest-energy state of
size-mismatched alloys is the chalcopyrite structure (ob-
served in GaAso 5Sbo 5), not the CP structure seen in
GaInP2, whereas for the lattice-matched Alp 5Gap 5As al-
loy, the next states are the (111)-ordered structures and
the(')Tj ET(the)Tj ET BT /Xd ((114 38attice-maom)Tj ET BT /Xi2 8.9 Tf 111.56 376.56 Td (alloy,)Tj ET BT /Xi2 9.41 Tf 139.33 377.11 Td (not)Tj ET

then

"frozen") bulk energetics indicates that this would not re-
sult in the structures that are actually observed for
Gap 5Inp 5P and Alp 5Gap 5AS.
(iii) In the case of lattice-mismatched systems, coherent
epitaxial growth could stabilize the homogeneous phase
by the of the constituents. Here, one
considers the case where the growing film is sufficiently
thin so that

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(a)

0.. 0
0::

(c)

VNC;; 'I

::: 0 0:::
''. 0.. 0

(d)

/

.

.
'6 '. 0
:::, 0 0.'
. 0.'0

(e)

,

.

''0 '.

. 0

''. 0.

'~0

0 Ga surface
Q In surface
~ P subsurface
[010]

= [100]

FIG. 2. Surface atomic arrangements for the 2X2 surface cell. See Table I for the description of the bulk structures that can be obtained by different stacking of these surface unit cells.

transfer between opposite surfaces. The single-surface
slab is computationally more expensive but it allows re-laxations five layers below the surface and was used to check oux results. We use the first-principles local-
density pseudopotential method with the

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TABLE II. Surface energies for the varoius GaInP2/GaAs (001) reconstruction modes discussed in the text. The energies are in meV per surface atom relative to the unreconstructed a +b (phase

+(001)

svaroius

per intotext. are modes the modes modes

+

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buckling, but it breaks the symmetry of the other sur-faces. Buckling

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geometries are tabulated in Fig. 6 [see (d') and (e*)]. We would expect the ionized surfaces to have dimer geometries similar to the low dimer geometries for the neutral surfaces. Comparing the two, we see that the bond lengths are closely preserved

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Ga

0.

(0.
0.

Ga

0.

1

(0.5
0.9

9

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Dimer
type

Al up
Ga up

0
0

Surface type
d

38i11 9.26 Tf 451.2.

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(Table II) of the surface reconstructions found in the
first-principles calculations, induces a strong preference
for CPz layer ordering at h

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