PHYSICAL REVIEWER 8 VOLUME 37, NUMBER 6 15 FEBRUARY 1988-II Stability of bulk and yseudomoryhic epitaxial semiconductors and their alloys

A. A. Mbaye, ' D. M. Wood, and Alex

STABILITY OF BULK AND PSEUDOMORPHIC EPITAXIAL... 3009

1.2

Bulk artd

Epitaxial Systems

~ $200

' 1000

800

600

400

P 200

0

l t I t I
I

'

e I

t

I
4

5.45 5.55 5.65 5.75 5.85

GeP InP

Substrate Lattice Parameter a, (A)
FIG. 1. Deformation energy of cubic (dashed lines) and
tetragonally distorted epitaxial (solid lines) GaP and InP, (a),

and dependence of c/a upon substrate lattice parameter a„(b).
Shaded area indicates substrate strain. The inset shows the
zinc-blende structure.

ordering vectors. There are eight such A„84 „C4sys-tems we wish to consider: for n =0 and 4 we have the

binary end-point zinc-blende (F43m space group) com-pounds A C and BC (inset to Fig. 1); for n =2 we have the 50%-50% compound ABC2 with either a CuAu-I cation (A,B) sublattice [corresponding to the ordering

co 2e2 2Q
V
4.8
0.25

~ Qs4) Q
0.23
0.22

Epitaxial Systems
CLIAM-I CHAL. COPYRITK

(a) (d)

(b) -' U

239.08 372 Tf 49.84 353.67 Td (cation)T.38 471.11 Td (cub4ms)Tj ET BT /Xi1 5.1 8.f 493 2(c)/.11 Td (cub4ms)249.84 3531 3 (e222 611.d /Xi1 10.21 Tf 108.042 364

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~

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InP

3010 A. A. MBAYE, D. M. %'OOD, AND ALEX ZUNGER 37

TABLE I. Primitive translation vectors and atomic coordinates [in Cartesian coordinates (x,y, z)]
for the Sve fcc Landau-Lifshitz structures

37 STABILITY OF BULK AND PSEUDOMORPHIC EPITAXIAL.

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w
= '+—[2(Rac

—R~2, c) (Rttc

—Ra(, c)]/rt

a

the Al

—C (A2

—C} bonds representing —, ' (

—', } of

A

—C

bonds present. Hence, the degrees of freedom are I a, g, u, w [; for the undistorted famatinite structure,

'go=2 Up=

4

and mo= s.

1

B. SigniScance of cell-internal degrees of freedom
for structural stability

%'hen g=go and the

C atom is at the center of the

tetrahedron formed by its

A and

B neighbors [i.e.

,

u
=uo,

u =uo, and

w =wo in Eqs. (1)-(4)] one has equal
bond lengths R„c=Rt(c=&3a/4. These undistorted bond lengths are generally different from the "ideal" bond lengths d„c=~3a„c/4and dec

=~3asc /4 of the
binary zinc-blende structures AC and BC, respectively. These difFerences, as well as the corresponding devia-tions from ideal tetrahedral bond angles 8 =109.5', set
up

a microscopic (cell-internal} strain energy proportion-
al to (8—8) and (R ti —d t(). These systems must lower the microscopic strain energy resulting from this failure to accommodate ideal bond configurations by ad-justing the internal degrees of freedom. The degree of
strain

37 STABILITY OF BULK AND PSEUDOMORPHIC EPITAXIAL... 3013

bulk versus epitaxial growth, random probabilities [Eq.
(18}] are sufficient. The observed mixing enthalpies at
high-temperature are customarily represented as

EZHD(x) =Ox(1—x) (19)

where Q, independent of temperature in this limit, is the
"interaction parameter. " Using Eq. (17) we may write hH (x, T} 0= '
=Q)+Q2+Q3, x(1—x)
where the contribution from the bulk formation enthal-pies is

E' '"'(a,)=E' '"'(A„B~ „C4,a„c(a,},tu(a,)I). (25)
In analogy with the bulk case (Sec. III A), one can define partially relaxed energies for epitaxial systems, by keep-ing certain structural parameters fixed.
Under pseudomorphic epitaxial conditions,

A. A,. MBAYE, D. M. %GOD, AND ALEX ZUNQER 37

TABLE II. Calculated minimum (min) energy lattice parameter (a;„)in A and

37 STABILITY OF BULK AND PSEUDOMORPHIC EPITAXIAL... 301S

yielding, in analogy with Eq. (12}for the bulk case,

c, (a„x)=
y. P„(x,T)C',",'a,'",'

(37)

Inserting ceq(a,,x) into Eq. (32) and using Eq. (34), we
may write the epitaxial mixing enthalpy as

5HD(a„x,T)=b,E[c,q(a„x)]
= g P„(x,T)5H'"'(a,)
+ Q P„(x,T)F„'r'[c,(x,a,)]. (38)

As described in Eqs. (15} and (17) for the bulk case, the effects of alloy-induced cluster relaxation

A. A. MBAYE, D. M. %'OOD, AND ALEX ZUNGER 37

the same structure ddt' '=

—25 meV/atom-pair, for

CdHgTez (Ref. 32} hH' '=+6.

1 meV/atom-pair, for
zinc-blende SiGe (Refs. 16 and 20) hH

=
+17.

8

meV/pair but for SiC in the same structure' ' hH

=

—659 meV/pair (+0.23,

—0.58,

STABILITY OF BULK AND PSEUDOMORPHIC EPITAXIAL... 3017

Bulk Systems
CuAu- l CHALCOPYRITE

1.8

~

0.25

024- U
0.23

(e)-

gl

~e ~1000 i („„) (Uo r}o)

(«' 9eqI
iu o

800-

O I 800-',

W ~

(uD 7') CQ gO)
400- '.
. (~., v.,)
E

1& r 9'VI

~ ~ 200- ---.
--. (0„,go)- I
Q 0
5.45 5.55 5.65 5.75 5.85 5.55 5.65 5.75 5.85
GgP .
o InP Bulk Lattice Parameter (A)
FIG. 4. In analogy with Fig. 2 (see caption),

3018 A. A. MSAYE, D. M. %OOD, AND AI.EX ZUNGER 37

even for structures characterized by a

STABILITY OF SULK AND PSEUDOMORPHIC EPITAXIAL.

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A. Bond lengths of bulk disord«ed alloys

Recent extended x-ray absorption fine structure (EX-

AFS) experiments showed average bond lengths R zc(x) and Rzz (x) in pseudobinary adamantine alloys
very close to the corresponding ideal bond lengths d„c
and daz. This behavior has been explained by Martins
and Zunger on the basis of

a structural optimization of
a valence force field. This theoretical Inodel also pre-
dicted successfully a number of alloy and impurity bond lengths not measured at that time.
%e have calculated the concentration variation of the
alloy bond lengths of Eq. (24}, appropriate for

a high-

temperature alloy. For each volume V,„(x)we use the
fully optimized (ri,

,u,

) bond lengths of the ordered
structures. These are averaged with the weights of Eq. (18), producing R„c(x)and Rgb(x} depicted in Fig. 7.
Figure

7 also shows the values of the ideal bond lengths
do,

p

and
d i„pas dashed horizontal lines. The results of Martins and Zunger for the dilute impurity limits GaP:In and InP:Ga (solid circles in Fig.

7 labeled MZ}
are seen to be in good agreement with our results extra-

polated to x=0 (for Ri p) aild x =1 (foi' Ro p}. In
Fig. '7 the equilibrium bond lengths Rz"c and E.zc for
the corresponding ordered phases (zinc blende, chalcopy-rite, famatinite) at the stoichiometric compositions X„=n/4are shown as squares.
Our calculated alloy bond lengths clearly show

a bi-

modal distribution, despite the fact that the V,q(X

3020 A. A. MBAYE, D. M. %'OOD, AND ALEX ZUNGER 37

parentheses) in Eq. (17) using random probabilities and
the equation of states [Eq. (8)] for the five ordered
phases, keeping

E =0 in both cases. %e then examine
the efFects of alloy-induced cluster relaxation (E &0).
In Fig.

8 we show the enthalpies of formation of or-
dered ternary compounds as diamonds, together with re-sults for the disordered bulk alloy. In all cases we note that the mixing enthalpy of the disordered alloy is posi-tive, i.e., it is unstable with respect

37 STASH ITY OP BULK AND PSEUDOMORPHIC EPITAXIAL... 3021

da 2.55 - "in-r

Epitaxial Alloy

Bond Lengths {a

Plane
X

Plane

Epitaxial Nloy INixing Knthalpy SH (x,a,)

Olfe

2.50
40

2AS

'Q

2.40,;
l5

Ir

2.35- d Ga-po

2.30
0.00
GaII

I i i

0.25 0.50 0.75

Coinposltion x

1.00
InP

FIG. 9. In analogy with Fig. 7 (see caption), bond lengths

for the epitaxial random Ga„ln& „Palloy and ordered com-
pounds

37 STABILITY OF BULK AND PSEUDOMORPHIC EPITAXIAL.

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(iv) Under pseudomorphic epitaxial growth conditions,
one degree of freedom

—the cell dimension parallel to
the substrate

—is externally fixed. This results in "sub-
strate strain energy" [Eq. (27)]. Relative epitaxial sta-bility of di8'erent structures is then determined by the ability of the system to lower its strain through relaxa-tion of the remaining degrees of freedom. %bile binary AC or BC compounds can do so only by tetragonally de-forming (Fig. 1), ternary systems can also utilize their cell-internal degrees of freedom to lower their

3024 A. A. MBAYE, D. N. %OQD, AND ALEX ZUNGER

ally that of Cu~AsS&, see F. Marumo, and %. Nowachi, Z.
Krist. j.24, 1 (1967). To avoid confusion, we specify in Table
I and Eqs. (1)-(4) what we mean by these structures; the
reader should, however, be aware of the possible uncertainty
in assigning the mineral names luzonite and famatinite to
these space groups. %e thank Dr. D. Cahen for discussing
these