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Strain energy and stability of Si-Ge compounds, alloys, and superlattices

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First-principles total-energy pseudopotential calculations are carried out for Si, Ge, zinc-blende-structure SiGe, (Si2)~/(Ge2)~ superlattices in various

STRAIN ENERGY AND STABILITY OF Si-Ge COMPOUNDS,... 1665

sufficient structural freedom to satisfy simultaneously the constraints [r;JI =[R;J] and [0;JkI= [8;~kI. Such

1666 JAMES E. BERNARD AND ALEX ZUNGER

diamond structure, with a particular choice of "phase"
between the two SL's. As a check of the quality of this
SQS, we also calculate the strain energy of a number of
large random supercells, where 1000 Si and Ge atoms are
distributed randomly on a diamondlike lattice, and the
relaxed energies are averaged over many distinct
configurations of the random system. We find that a cal-
culation on SQS-8, with just eight atoms per cell, closely
reproduces the results of this direct simulation with 1000
atoms per cell, thus substantiating the SQS construct.
These results are discussed in Sec. IV.

The complete analysis of SL formation enthalpies and
random alloy mixing enthalpies in terms of our model of
Eqs. (5) and (6) then permits assessment of thermodynam-ic stability of various phases. This is discussed in Sec. VI.

III. METHOD OF CALCULATION

A. First-principles pseudopotential calculations

Our first-principles self-consistent plane-wave pseudo-
potential calculations were done in the local-density ap-
proximation with a plane-wave energy cutoff of 20 Ry,
using in all cases the equivalent of 10 special k points in
the irreducible part of the diamond Brillouin zone. The
use of equivalent basis sets, k-point sampling, and self-
consistency for all structures results in a relatiue precision
of AH's for near-equilibrium structures of about 0.1
MeV/atom (whereas absolute accuracy is not as good).
For determination of the AVFF parameters, we did
four sets of seven total-energy calculations for each of the
three materials, Si, Ge, and zinc-blende-structure SiGe:
one set scanning the volume (maintaining a cubic cell),
and three sets being done under coherent epitaxial condi-tions, where the substrate lattice constant in the (001) plane was held at approximately the equilibrium lattice
constant of Si, Ge, or their average, and the c/a ratio was
varied. The range of the cubic scans was about +15% of
the equilibrium volume, and that of the epitaxial scans
was +9%%uo in the c /a ratio.

In a number of the first-principles calculations the
structural distortions caused the materials to become me-

tallic. In addition, it is not possible to preserve absolute
equivalence in k-point sampling under the distortions in-volved in the scans (we distort the sampling mesh along with the unit cell, to preserve both the number of mesh points and the topology of the mesh in the full Brillouin zone). As a result of these and other sources of noise in the first-principles scans, all fits of these results were done

with weights applied to the scan points, giving gradually
decreasing weight to points further from the energy
minimum, and reducing the weight for metallic cases by
an additional factor of 2. All fits were done using g
minimization.

Table I summarizes the results of the scans. The equi-
librium lattice constants were determined by fitting the
results of the volume (cubic) scans to a Birch equation of
state. ' The bulk moduli and epitaxial strain-reduction
factors

E(Ci, a„c,q

)—E(a,q

)

q(G)= E(Cx,a„c=a,)—E(a,q

)

(7)

(where the subscript "eq" denotes equilibrium values, and the c-axis dependence is made explicit for the epitaxial
energies) were determined from the second-order elastic
constants C» and C&2 resulting from fitting to a third-
order elastic model.

oTf 77.89 276. 9.26 Tf i3 9.67 T.44 Td (equilibrium)Tj ET BT /Xi3 9.26 Tf 442.89 514.89 Td (c-axis)Tj ET BT /Xi3 8.83 Tf 012.89 514.

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c/a6)

scans

toa third(order)Tj ET BT /Xi3 932 Tf 408.674393.33 Td (elastic)Tj ET B terms

C»

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STRAIN ENERGY AND STABILITY OF Si-Ge COMPOUNDS,... 1669

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8

E

U) I
CP
~ ~

(0

H1

RH2
4

(110)
(001)

m

1 I I
I

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I

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I

{8) (Si&)&/Ge&)& on

lattice-matched
substrate as = a

7.47

7.05
5.89

)4.43

12.07
11.70

7.98

RH2/(111)

RH1/(11 1)
(110)/(110)

(001)/(001)

R

(b)
(Sl&)&/(Ge&)& on
Si substrate

- 12

- 10

Z8

0,—~

I I I I I I I I I

5 10 15 10 5

-0

0

FIG. 2. Strain energy of SiGe superlattices and the random alloy on (a)

STRAIN ENERGY AND STABILITY OF Si-Gc COMPOUNDS,... 1671

er than the standard deviation of the large supercell re-
sults.

Comparison with the SL results of Figs. 2 and 3 shows that, while a number of ordered epitaxial SiGe structures on Si have lower strain energy than their strained constit-

uents, only the ZB and RH1 p =1 structures also have
lower strain energy than the random alloy (modeled by the SQS) of the same composition.

V. FORMALISM AND RESULTS
FOR CHEMICAL ENERGIES

E,i„(cr)=g D~J~II~(o),

F

(17)

Having described in Sec. IV the microscopic strain en-ergies EEMs of the various Si/Ge SL's, we turn now to the second component of the formation enthalpy hH of Eq. (5), namely, the chemical energy EE,h,. We base our calculation on the technique of cluster expansion, wherein a lattice energy (here b,E,„,) is represented as an expansion in a complete orthogonal set of "cluster
functions, " with coefficients that represent the values of
that quantity for the clusters. The total chemical energy (per atom) of a configuration o (i.e., a given arrangement of Si and Ge atoms on the N sites of a basic lattice with the diamond structure) is represented as
2Ã

E,„,

1672 JAMES E. BERNARD AND ALEX ZUNGER

TABLE VI. Lattice-averaged pseudospin products IIk [Eq. (18)]for several structures on the diamond lattice. II2 give the pair terms for atoms separated by an mth-neighbor distance, while H4 give four-body terms characterized by mth-neighbor separations. For all structures Hp p= 1, and for all structures included in the table, Hk p=0, for k for odd. Also included is P», defined in Eq. (20). For

STRAIN ENERGY AND STABILITY OF Si-Ge COMPOUNDS,... 1673

TABLE VIII ~ Results of cluster expansions based on the pseudopotential (PS) results of Ref. 40 for 11 SiGe structures in both the unrelaxed (ideal atomic positions) and relaxed configurations. Superlat-tices are denoted by the orientation Cx (or RHn for the [111]SL's), in parentheses, the numbers of Si and Ge monolayers, respectively. Values for those structures used as input for the determination of the cluster energies are enclosed in parentheses; the rest are predictions and are to be compared with the direct pseudopotential results. The unrelaxed systems are reproduced well by a three-term cluster ex-pansion including only Jo,J», and J2 2, whereas the error in a similar three-term cluster expansion of the relaxed systems is far larger. In order to achieve comparable convergence in the cluster expansion for the relaxed systems,

STRAIN ENERGY AND STABILITY OF Si-Ge COMPOUNDS,... 1675

of incomplete relaxation of RH1 by Ciraci and Batra, the smaller basis set used by them, and residual errors in our model calculation. A direct first-principles calculation

1676 JAMES E. BERNARD AND ALEX ZUNGER

7.

RH2b

O

C0

E
Ul

I

5- ted (001)

c 3-
CO

CO

2-

RH1b

RH1a

0 5 10 15 20 25 30

FIG. 4. Strain energy of [001]-oriented (Si2)q /(SiGe)q super-lattices on a [001]-oriented Si substrate. The variants a and b arise from symmetry breaking of the SiGe structures caused by the presence of Si/SiGe interfaces and are described in the text.
The curve labeled "phase-separated" has maximally phase-
separated (along [001])SiGe alternating with Si.

near the interface), the strain energy per atom of the SiGe layer alone is essentially twice that shown in Fig. 4. A
similar statement applies to the chemical energy AEcc
shown in Table X. In the q —+ao limit, the variants be-
come degenerate, and the formation enthalpy per atom of
SiGe is just the result obtained from a calculation of SiGe
on a virtual (001) Si substrate (Fig. 2). The total energies
of conventional virtual-substrate calculations are

recovered to within l%%uo by q =24. For all q, the RHla
variant has slightly lower strain energy tha33 Td (of)Tj ET BT /Xi13 729.11 T8.69 Tf 106.(ly)Tj ET BT /Xi13 9 f 271.33 339.56 Td (RH)Tj ET T

Sie

variantssubstrat1Xi13 9.1 88ge104.89 370.78 Td (irtual)T BT /Xi18i13 8.87 f 1tf 206.44 457

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arg.

STRAIN ENERGY AND STABILITY OF Si-Ge COMPOUNDS,... 1677

tice points increases linearly with the repeat period (4p) of

STRAIN ENERGY AND STABILITY OF Si-Ge COMPOUNDS,...

tion enthalpy into a bulklike strain term analogous to our EEcs and an interfacelike term