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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

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

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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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E
O

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8

E

U) I
CP
~ ~

(0

H1

RH2
4

(110)
(001)

m

1 I I
I

I
I

I
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)

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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,„,

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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

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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,

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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

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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 than the RH1b variant, though the largest splitting shown in Fig. 4, for q =4, is less than 0.3 meV/atom, only about l%%uo of kT at
room temperature.

The variants are energetically distinguished only by their interface energies, and the strain (SR) and chemical

(CE) contributions to these are always of opposite sign, so that their sum is generally smaller in magnitude than ei-ther contribution. Hence, the distinction between the
variants is smaller in the total interface energies than in
either contribution. We note the exceptionally large
(001) total interface energies of RH2a and RH2b. A consequence of this is that in thin layers of SiGe on (001) Si, the energy difference between RH1 and RH2 will be
reduced. This is especially evident for very small q, as is
shown in Table XI. Indeed, for q =1 we find that the to-
tal formation energy of the RH2a variant is very slightly
lower than that of RH1a, while the two b variants are de-generate by virtue of being structurally equivalent. How-
ever, for q(4 the identities of the SiGe phases are not
well defined because the slab does not contain complete unit cells of them.

We conclude that for sufficiently thick (large q) films
substrate interface effects are negligible in these struc-
tures when grown on (001) substrates, and will not alter
the conclusions drawn from calculations based on the use

of virtual substrates. Indeed, for the systems considered
in Fig. 4 and Table XI, the q =4 energy order is exactly the same as that in the q~ac (virtual substrate) limit.
We also conclude that well-separated Si/SiGe interfaces
cannot help to explain the discrepancy between calculat-
ed order-disorder transition temperatures and that ob-
served by Ourmazd and Bean' in a structure similar to our q =28 Si/SiGe SL.
It is useful to consider under what circumstances the film-substrate interface interactions omitted by the com-
mon use of a virtual substrate might become more impor-
tant. In particular, we consider the fact that the lattice
registry imposed by a virtual substrate does not necessari-ly imply atomic registry at the interface. This is of no concern when lattice registry implies atomic registry, as is the case for SL's grown on "native" substrates, i.e.,
substrates whose surface normal G, is parallel (or nearly
so) to the SL stacking direction G. However, for SL's
grown on "foreign" substrates, i.e., with G, not parallel
to G, such as (110) or (111) SiGe SL's grown on (001) Si
substrates, the number of interface atoms not lying at lat-

TABLE X. Interfacial chemical (IcE), strain-relief (IsR), and total (I) energies (meV/primitive-cell interface) in the q~ ~ limit (i.e., isolated interfaces), constituent chemical energies EEcc (meV/atom), and constituent strain energies AEcs (meV/atom) for vari-ous [001]-oriented A /B SL's on a (001) Si substrate. Here 2 consists of q double layers of Si, Ge, or SiGe in one of the phases RH1 or RH2, and B consists of q double layers of SiGe in one of the phases RH1, RH2, SQS-8 (quasirandom), or phase separated along [001] with p=q/2 (PS). Hence, one or both of the "constituents" contributing to bEcc and bEcs here is SiGe. The interface unit cell is 2X 1, and all interfaces are (001) oriented. Note that there is no a/b variant distinction for the Si/Ge interface (Si/PS) or the
RH1/RH2 interface. All rhombohedral structures included here are the p

=1 SL. APB denotes a (001)-oriented antiphase boundary.
Interface

Si/RH1
Si/RH2
Si/SQS-8
Si/PS
Ge/RH1
Ge/RH2
RH1 APB
RH2 APB
RH1/RH2

Ic(E)(M)

3.76
3.76
3.76

APM)#r (A BT /Xi))Tj E6234 127.11 Tf 5126 Tf 130.44 360.333Sf 300.67 T B19.11 Td (total)T8T /Xi) 76

SiG9Tj ET BT /Xi13 11.046Tf 194.6 Td 89 Td (SiG82)Tj ET BT /Xi13 13 71.78 2 21 Td (interfaceq)Tj ET BT /Xi13 261 Td (t9189.1129 Td (SiG1Tj ET BT /Xi13 11.0 Tf 19 c

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

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pansion based on first-principles results for the two topo-

logically unconstrained structures ZB and RH1 p=1. Values for these quantities are given in Tables IV and VIII, the latter containing also directly calculated first-principles results for selected structures. The epitaxial formation enthalpy 5H(p, G, a,

) (taken with respect to
constituents coherent with the substrate) is given by Eq. (15), and its sign depends on the signs and magnitudes of its two components, both of which are purely interfacial
in nature.

Considering only the strain energy of (Siz)~/(Gez)~ SL's, we found that (i) for long perio-d SL's, the stability sequence is like that in lattice-mismatched pseudobinary III-V SL's (001)

)(110)

)(111), refiecting the

orientation-dependent constituent strain EEcs; yet (ii) for short-period SL's the interfacial strain relaxation IsR favors the RH1 form of the (111)SL over (001) and (110), while the RH2 form has the highest energy; (iii) only the ZB and p=1 RH1 structures have lower strain energy that the random alloy, and this is so both for a, =a and
a,

=

a s, and

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