34

STABILITY,
ELECTRONIC

STRUCTURE, AND

PHASE DIAGRAMS OF
NOVEL INTER -

SEMICONDUCTOR
COMPOUNDS

L . G. Ferreira,

S.-H. Wei, and

Alex Zunger

SOLAR ENERGY RESEARCH INSTITUTE
GOLDEN, COLORADO 80401

Summary

High -technology electronic devices are based on highly specialized core materials that make their operation pos-
sible : semiconductors. Unfortunately, the range of mate-

rial properties that make high-technology devices work
is extremely narrow, since the sheer number of useful
se miconductors is small. Hence, a major challenge has
been to predict and develop new, potentially useful
se miconductors. We describe here how the use of state-
of -the-art techniques in both quantum and statistical
mechanics can lead

and

t m (and)Tj 0.0001210.00018143 0 0 9.7296.56 307.2 Tm (use)Tjuctors.

o 0 (Unfortun)Tj -24 4 Tm7Tm (h 0 9.lloy3 99.369of-the-arj 0.0 0 7.

35

Pig . 1 Structural
des cription of the new,
inter se miconductor
phases .

stabler than the phase-separated systems (Dandrea et al.,
1990).
Since our original prediction, more than 20 obser-
vations of such long-range, ordered, inter-semicon-

ductor compounds have been made (see Zunger and
Wood , 1989, and compilation of references therein). It
now appears that this phenomenon of long-range, or-
dered , inter-semiconductor phases is likely to be the rule

rather than the exception in semiconductor physics. It is obvious that direct calculations of the internal
energies of such systems will not suffice to model their

properties and stabilities. First, these are often stable

only at finite temperatures, the

to calculate directly the energies of such a large number.
of configurations in an effort to delineate the stability of

ordered and

where

Here , Ni is the occupation number of level i below the
Fer mi energy EF; p(r) is the electronic charge density ob-
tained from the self-consistent single-particle wave func-

tions ; Za is the atomic number of atom a at Ra; V 1 (Ra) is the coulomb potential at Ra due to all elec-
trons and nuclei except the charge Za at Ra; V, and Vxc are, respectively, the coulomb and electronic ex-

change-correlation potentials; and Exc is the exchange-

correlation energy density. Solution of Eq. (15) requires first the solution of the Schrodinger equation, including
(three-dimensional) coulomb, exchange, and correlation.
This is the single most expensive step in the calculation.
The charge density is determined self-consistendy and variationally from the semirelativistic (i.e., retaining all

relativisti c terms but spin-orbit interactions) local density Hamiltonian. For each unit cell volume V, we minimize
the total energy with respect to the cell-internal atomic coordinates, thereby obtaining relaxed energies. To en-sure effective numerical cancellation of systematic errors
in Eq. (14), we use for AnBffl’ AnAm, and BnBm precisely

equivalent basis sets and integration methods, and
sa mple the Brillouin zone by sets of wave-vectors k
whi ch are geometrically equivalent in AnBm, AnAm, and
23~6~. We use for the zincblende structure the two spe-cial k points (Chadi and Cohen, 1973) and equivalent k

points are used for all other structures. Convergence tests with respect to k point sampling show that the
error in AE is less than 5 meV per four atoms.

COMPUTATIONAL DIFFICULTIES IN THE
Q UANTUM MECHANICAL STEP
The ex cess total energy of structure s, Eq. (14), is of the
ord er of ---10-2 eV per atom; difference of excess en-
ergies between different structures are of the same

ord er or s maller. Yet, the directly calculated total elec-
tron plus ion energy, E in Eq. (14), is of the order 105 to
101 eV per atom. Hence, extremely converged and pre-
cise calculations are needed. This energy is obtained by solving a Schr6dinger equation with basis sets of the
order of Nb = 103 basis functions. Storage

ever , our iterative diagonalization algorithm described

by Wood and

also require that the spin of the first sublattice is + 1

(atom B). After occupying the M sublattices with atoms A or
B , it may happen that the translational symmetry of the

resulting configuration is larger than what was assumed
by the unit vector f all. For instance, in an fcc-based con-

figuration with unit vectors al = (2,0,0), a2 = (0,2,0), and a3 = (0,0,2) there are M = 4 sublattices with bases
bI = (0,0,0), b2 = (1,1,0), 0,2,0 .4 Tm (8 Tm (f804 639.84 Tm 9.4228.1 0 0i.96 0 0.28 Tm 13603.651 TT8 Tm (4852ue5756. 3.21.44 642.240o9b2.2401 639.8

belongs to the

full fcc group the translation

group generated f Then the extra-translation

The

ve ctor must correspond is the

to one of the basis ve ctors f translation b; also be-

group of the

for

all basis ve ctors b;,

In other words, bi bi bj

the sa me

or

the If Eq. (50) and cer-
the configuration has higher translational
metry must be discarded.
given a triad of vectors,

46

ter ms (Ferreira, Wei, and Zunger, 1989). We next dis-
cuss the salient features of the results.

THE Q UANTUM-MECHANICAL
INTERACTION ENERGIES

Using the LAPW calculated equations of state fAE(sV)l for the eight special periodic structures (Fig. 1) and
Eq . (16), we obtain the volume-dependent interaction energies depi cted in Figure

48

Fig . 5 Calculated
redu ced enthalpy for the

disordered alloy (solid
lines), see Eq. (53), and
for ordered compounds

(diamonds), see Eq. (54)

se miconductor alloys, as observed in liquid-phase epitaxy

growth (Nakayama and Fujita, 1986) of Inl_xGaxAs and

in vapor growth (Jen, Cherng, and Stringfellow, 1986,
1987) of GaSbl-xAsx’

Second, for size-matched alloys, the disordered alloy has a lower enthalpy than any of the simple ordered
structures studied; hence, no therrr~odynamically mandated ordering is expected in size-matched semiconductor alloys. The CuAuI-like ordering observed by Kuan et al. (1985) in

Al 1_xGaxAs is likely to be surface-induced.

Third , the CuPt ordering recently observed in epi- taxial growth of size-mismatched semiconductor alloys (see Fig. 1) is characterized by a considerably higher en-

thalpy than the -

thalps

binodal is the line in the (x,T) plane where the A-rich
and B -rich disordered phases have equal chemical po-

tentials)JL. The spinodal line describes the limit of meta-

stability of the disordered phase when d2Fldx2 = dp/Ux = 0, F being the free energy. In all cases, we find that

the thermodynamically stable ground state corresponds to phase separation. The phase diagrams are generally asymmetric with respect to x = 1/2.

Experi mental data on the solid-state part of semi-
conductor alloy phase diagrams are fragmentary: al-

though detailed data exist on the high-temperature liq- uidus and solidus lines, the low atomic diffusion con-
stants at lower temperatures make such studies in solid
se miconductors difficult. The recent data of Ishida et al.

(1988) for GaSb 1 _x Asx shown in Figm.506 30 60c00119 155.04 m 9.4228 2570 0 9.1 256.xm135.84 51j 0.000132.96 M4625 168.96 50

49

Fig . 7 Calculated phase
diagra ms for the 11-VI

alloys (a) Cd,- .H9. Te, (b)

Hg , _=2n,~Te, and (c) Cd,_...Zn.. Te

and phase separation. This

51

and fl = 948.5059 meV (four atoms).

The Monte Carlo runs were made using single spin-flip kinetics (Styre, Phani, and Lebowitz, 1986). We

used a

52

find the ground states supported by this Hamiltonian.

The stability analysis is most simply made in the (E,G)
for malism, where the configuration a has the energy given by Eq . (22). We will refer to the second term of this equation as the &dquo;chemical&dquo; energy ~E~,~em(Q). To
establish the stability conditions,

53

position y between two vertices of the GSL (say, 1 and 2
in Fig. 3). In this case the energy change associated with
rea ction (56) is purely elastic, that is,

Since by Eq. (20) d2G/dx2 = -Z(x) where Z(x) > 0 by Eq. (21b), this energy change must be negative, that is,
and the rea ction (56) proceeds to the right (decomposi-
tion). This process can continue until one reaches a
composition y corresponding to a vertice in the GSL sur-

rounded by two minima (e.g., vertex 2 surrounded by vertices 1 and 3 in Fig. 3). Now the energy change asso-
ciated with reaction (56) has both elastic and chemical contributions. By Eq. (57) we have

Since the second term (‘xchemical&dquo;) is positive and linear
in the concentration fluctuation w, it will overwhelm the

el asti c term (quadratic in w) for small w. In this case 3M.
is positive and reaction (56) proceeds to the left: com-

pound formation is favored. Hence, the local minima of ~E(~~ (Fig. 3) correspond to metastable long-range ord~ri-ng. We conclude that at a general composition x, phase sep- aration will occur until a special composition X2 is en-

countered, at which point DE (X~) becomes locally stable

against composition fluctuations. In perfect equilibrium at X2, the system will overcome the barriers evident in

Figure 3 and produce the true phase-separated ground state. However, at sufficiently low temperatures the

syste m cannot surmount these barriers and will exhibit
long -range ordering in the phases shown in Table 4.

This de monstrates that metastable long-range ordering found in our phase diagram calculations is a conse-

quence of the coexistence of negative chemical energies with (larger), positive elastic energies.demonstrates ive e

Table 5

Limiting Temperature T, of Stability for Some GaSbAs Phases Belonging to the Ground-State Line of Chemical Energies

Calculations were made with Eq.122). We characterize each structure by the number and type of independent figures appearing n it Here, Q means a tetrahedron, T a triangle, Pl a wit34

dinated ato ms. Growth techniques involving a free sur-

fa ce (e.g., molecular-beam epitaxy) would have a dif-
ferent thermodynamics owing to the lower symmetry

(e.g., surface clusters are likely to have different energies than clusters surrounded by atoms in all three direc-
tions). Indeed, in the presence of surface reconstruction
effe cts, the energy-minimizing structure can be qualita-
tively different from that obtained by minimizing the
bulk energy. To the extent that coverage of the surface
free zes in the surface-stable structure, it could persist
metastably to macroscopic dimensions. The fact that
growth te chniques that involve free surfaces 6 0 0 9.726.2286 0c 0 0 9.1189 2 Tm (that)Tj 10 9.726dm (thauM 9.7uc 6.8 t011 Tb 557

56

Ferreira , L. G., Wei, S.-H.,

and Zunger, A. 1989. Phys. Rev. B 40:3197.
Finel , A., and Ducastelle, F. 1984. Mat. Res. Soc.
Symp. Proc. 21:293.

Hohenberg , P., and Kohn, W. 1964. Phys. Rev. 136.

Ih m, J., Zunger, A., and
Cohen, M. L. 1979. J. Phys. C 12:4409.
Ishida , K., Shumiya, T.,
No mura, T., Ohtani, H.,

and Nishi zawa, T. 1988. J. Less Comm. Metals 142:135.

Jen, H. R., Cherng, M. J., and Stringfellow, G. B.

1986. Appl. Phys. Lett.
48:1603.

Jen, H. R., Cherng, M. J., and Stringfellow, G. B.
1987. J. Grystal Growth

85:175.

Kana mori, J., and
Kakehashi , Y. 1977. J. Physique 38(7):274.

Kikuchi, R. 1951. Phys. Rev. 81:988.

Kikuchi, R. 1974. J.

Chem.

Phys . 60:1071.

Kikuchi, R., Sanchez, J. M.,

de Fontaine, D., and

Ya maguchi, H. 1980. Acta.
Metall . 28:651.

Kuan, T. S., Kuech, T. F.,

Wang , W. I., and Wilkie, E. L. 1985. Phys. Rev. Lett.
54:201.

Martins , J. L., and Zunger, A. 1986.

J. Mat. Res. 1:523.

Nakayama, H., and Fujita, H. 1986. In Proc. 12th in-
ternat . symp. on GaAs and

related cmnpounds, Inst.
Phys . Conf. Ser. 79, edited
by M. Fujimoto. London:

Institute of Physics, p. 289.

Panish , M. B., and Ilegems, M. 1972. Prog. Solid State
Chem. 7:39.

Sanchez, J. M., Ducastelle,

F ., and Gratias, D. 1984.
Physi ca Rev.

Z