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First-principles study of intervalley mixing: Ultrathin GaAs/GaP superlattices

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First-principles

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which an optical transition in such systems is direct or
pseudodirect, and to the degree to which it can be labeled
type

I or type II. We also present predictions for the op-
tical transition energies in (001) and (111)(GaP)„(GaAs)„
SL's (Tables

I and IV).
Previous work on intervalley mixings in SL's has been confined mainly to the (001) GaAs/Al Gai As
common-anion system. In such

a (001) SL geometry, the
underlying zinc-blende

X states are split into X' (which
folds to the SL zone center, and thus couples to the states
at

I there), and

X and X~ (which couple to each other
away from the SL zone center). Two basic questions have been attempted to be answered: (i) what is the strength of
the

I -X' coupling at the SL zone center, and (ii) are the intervalley couplings experienced by

X and X', such as
to cause the X'~ SL level to lie below the X' level (possi-bly making the SL indirect in k space), in spite of the
transverse

X

~ mass being lighter than its longitudinal X'
counterpart. Regarding (i), understanding the

I

-X' in-

tervalley coupling is important since it directly affects

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on longer-period SL's. The band offset is obtained by
adding

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GaAs05 P05 VCA bands for [001] on as„b = a

(a) [001] 1=X, (b) [001] X„-X 111 111

X, X„ X„
[QQ1] Direction

y L111

FIG. 2. Bands of the VCA Ga(AsP) zinc-blende compound with lattice constant a along the (001) lines between the principal
band-edge valleys. The bands in (a) are folded to I, in (b) to M, and in (c) to L, in the SL zone.

VCA bands a.

The perturbative connection between ultrathin aXi4 8.42 Tf 390 479.96.04 Tf 368 537 Td (y)44 489.78„4 8.17 Tf 52s.67 Td (236 43

bands Bands bands cn (constant)Tj ET .1 Tf 86204868

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GaAs/A1As. As will be shown in Sec. IV, this is indeed
found in our calculations, with 1-eV splittings at M

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hc„=e(l „)—E(I 3„)
and the average energy is

(9)

(10)

Neglecting spin-orbit effects results in a triply degen-
erate I &5, zinc-blende valence-band maximum being split by the crystal field into a I 5, doublet and a I 3, singlet in
the strained binary compounds. The crystal-field (CF)
splitting is

the quasicubic model of Hopfield. In this approxima-tion, the heavy-hole state is

e(1 6 „)=e,„+—, '(b,, +b,c„),
while the light-hole and spin-split states mix to form two
states at

e(r7,)=E,„——, '(b...+b,cF)

(12)

Aligning these strained binary states on an absolute ener-gy scale as explained above, we find the following ener-
gies (all in eV): for GaAs, I ~, =0 and I 3„=—0.20, while for GaP, I ~,

= —0.52 and I 3„=—0.34 [see also Fig. 2(b)
of Ref. 42]. Including spin-orbit effects, the zinc-blende
valence-band maxima are composed of a I 8, doublet
(light-hole plus heavy-hole states) and a rz, spin-orbit split-off state. The I 8,-I 7, energy separation is defined as b... (where s.o. denotes spin orbit). The strain caused by lattice mismatch then splits the I 8„light- and heavy-
hole doublet and mixes the light-hole state with the I 7„
spin-split state. To quantitatively describe the interplay
of noncubic crystal fields and spin-orbit splittings, we use

(QQ1) Band Offsets: a,„b = a

2.2- 2.13

2. o
c

2.0 -X 1.96 6c

xy-. 1.8-

2.O3
~, 1.92
1.81

1.61

1.77 X6C-
1.70

1.6

6c 1.50 r-
GaAs

GaAs

strained B 0.

9I(0.)Tj ET BT /Xi8314.03 Tf 76.782168 Td (2-)Tj ET BT /Xi8 8.76 Tf 108.782.44 Td y-.(0

(0.)Tj ET BT /Xi8314.17 Tf177.11 149.22 Td (8-)Tj ET BT /Xi8 8.63 Tf 609.562405.22 Td y-.

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Penney theory, using the valence-band offset as

a fitting
parameter. However, rather than report the offsets of the strained constituent bands, they used an absolute deformation-potential model to relate these levels to those of their zinc-blende equilibria parent compounds.
Furthermore, they interpolated the offset to x=1 alloy
composition (i.e.

, GaP/GaAs). They thus reported

a

valence-band onset hE, =0.60+0.05 eV (with GaAs be-
ing higher) for the unstrained binary constituents. (This gives

a conduction-band offset EE,=0.23 eV.

) Recio
et ah. have performed

a very similar

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in the two halves of

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4

I n=3 (001) a „b —a

(a) I-(11

N

9- 2

0 I
As As As P P P

(b) I-(1)

0 I

I I I

As As As P P P

FIG. 8. xy planar average of the squared norm of the conduction-band minimum (a) and valence-band maximum (b)

wave functions of the n=3 (001) SL at a,„b=a. The planes of Ga atoms are represented by hatches along the abscissa. The dashed vertical line denotes the position of the interface.

functions and in terms of the magnitude

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TABLE II. Hamiltonian matrix (Xf~z»3, ~5 V~X;,~z»3,) that
determines the (001) SL conduction-band-edge levels at M. The costituena, zero/Xi13 8.57 Tf
542.33 72656911 142.56 Td
enatrnes the
the (001) the b1)
thate ransvershe
theeshe SLthe that tex SL

tex levels the rrix aVlX&3, ties
matrix
thrhee
matrix ro/X13 8.57 Tf
542855 Tf
272.675202.78 Td
vanish3,thate wro/Xi13 8.57 Tf

r

the
the
levels
the conduction-bans
level3,

levels the

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R n=3 (001) a„b-a

(a) R,"v)

cu 5-
9"

N

cu

As As As
10

(» F("

P P P

0

t0

As As As p P P

0
As As As P P

FIG. 12. xy planar average of the squared norm of the top
three valence-band wave functions of the n=3 (001) SL at R.
Note the extreme GaAs localization, due to the nearly infinite mass of the (001) L»& L»l dispersion. Note also that the usual
Kronig-Penney ground-state envelope function (being nodeless)
is now just the second lowest level, while the first and third states arise from even and odd single-node envelope functions, due to the intervalley mixing.

6. Comparison to GaAs/AlAs

It is instructive to compare these present results on
(GaP)„(GaAs)„SL's to similar results on the
(A1As)„(GaAs)„system. There are three reasons for this.

zinc-blende states with minimal 6k, resulting in their be-
ing 96%, 100%, and 93% localized in the GaAs half of the SL, respectively. The reason such extreme Kronig-
Penney-type behavior is seen even in these ultrathin
n=1 —3 systems here is because of the near-infinite mass of the band involved, resulting in near-vanishing energy
denominators. The wave-function plots of Fig. 12 show
the extreme GaAs localization of these states, but also
demonstrate a manner in which they do not behave as
typical single-valley Kronig-Penney states. This new be-
havior, due to two interacting heavy-mass valleys, is sim-ply that the usual Kronig-Penney ground state (having a nodeless envelope function) is now just the second-lowest SL state R z,', whereas the first- and third-lowest SL lev-
els

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TABLE III. Principal conduction-band edges of the (AlAs)„(GaAs)„(001) SL s, in relation to their parent VCA levels. In the cases of M and L, Ac is the splitting of the two degenerate VCA levels that fold there. All energies are in eV, and are measured with respect to the respective valence-band-

maximum state at I or I, including spin-orbit efFects. The asterisk in each column denotes the
conduction-band minimum. A gap correction of 0.92 eV was added to all calculated conduction-band
energies here. Note that the levels here differ slightly from those calculated in Ref. 22 (by less than 0.10 eV) and from those in Ref. 11 (by less than 0.14 eV) due to the different gap corrections performed in each case. (The states labeled I &„M&„and R &, here were labeled I 4„M4„and R4, in those two refer-
ences.)

Origin

VCA
Anion

X;,=2.14*
I),=2.28
Xq, =2.71

n=1
Cation

I), =2.06
I ~, =2.22
I I, =2.97

Pl =2
Anion

I „=2.09*
I „=2.21
I ~, =2.65

fl =3
Cation

I,=2.05*
I), =2.15
I"I, =2.48

X)~=2.14*

Xq~ =2.71

2M', =2.16

M(, =2.27
M2c =2.18

M2, =2.12
Mi, =2.15

2M5, =2.70

2M5, =2.08

Ml, =2.53
Mq, =2.83

0.905 0.031 0.296

L111 2 39

L] =2.39

R I, = 1.95*
Rq, =2.91

X),=2.35
X~, =2.37

R I, =2.19
Rq, =2.49

0.961 0.027 0.301

system like GaP/GaAs, however, the chemical part of
the SL ordering potential, 6V,h,,

is anion centered, and

the strain piece 5V„, due to the lattice mismatch adds p, character to 5V. This results in a much smaller splitting

at i.„,while the X" state that does split (the lower one
now) splits only half as much as in AIAs/GaAs (because its anion-s character is only half of the cation-s character of the upper X ~ state, which splits in the common-anion case). These arguments are very approximate, and are
meant only to suggest a probable connection between the
orbital character of various states and their resulting
splittings in common-anion or common-cation SL order-
ing.

At I, Table III shows that the three lowest SL
conduction-band levels evolve

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A. Structural properties

The nuclear coordinates in the (111) SL's are deter-
mined by a method analogous to that used for the (001)
systems. We again consider the SL in its bulk equilibri-
um configuration: its lattice constant a j perpendicular to
(111)is assumed to be equal to the average a of the lattice
constants of the GaP and GaAs zinc-blende equilibrium
structures, since we are again only considering equal-
period systems. A first guess at the nuclear coordinates within the SL is then obtained by first finding the equilib-
rium structures of the strained binary compounds (epitax-
ially constrained to a~ =a), and then layering these
strained binaries along [111]to form a SL. Calculation of
the self-consistent Hellmann-Feynman forces on the nu-
clei in the SL then allows for any correction to the cell in-terval degrees of freedom, while analysis of the stress on the SL unit cell similarly prescribes whether any further
[111] unit-cell distortion need be introduced. In the
present case, both of these checks implied that no further
relaxation of nuclear coordinates was required, and as in
the (001) case, the SL was exactly made simply of layers of strained binary constituents [the common Ga atom and the polar nature of (111) atomic planes making such a construction possible].
The nuclear coordinates of the strained binaries were
found as follows. After imposition of the epitaxial con-
straint a~ =a, there are two degrees of freedom left deter-
mining the structure of these binary compounds. One is
the lattice constant a», of the unit cell in the [111]direc-tion, which we shall describe by a trigonal distortion pa-rameter t)=a», /aj. The other is a cell internal degree of freedom g that describes the relative position of the two atoms in the unit cell, their separation being given by the vector (g, g, g)a~ /4. Minimizing the total energy of the binary compounds with respect to r) and g (with a~=a fixed) gives, for GaAs, g=1.032 and /=1.024, while for GaP we obtain q=0.978 and /=0. 986. Note that since the two q values average 1.005, there is [unlike in the (001) case] a very small (0.5%%uo) overall distortion of the SL unit cell along the growth direction. In summary, the g and a~ values given here completely determine the strain configurations of the elastically deformed G-aP and
GaAs constituents of these (111)SL's.

(111) Band Offsets: s,„b —'a

2.2-
111'
/

X

195
6C

/

1.78,'

1C
111

2. l6

1.79

2.21
/

2.11 111,/ 2 08 r'-,

/

1.94

81

/'l 11
/

"ec

L1C

1 73 1.74 -- X6 1.68
1.6-
1.58

GaAs

P ~ ZB eq.

1.49

GaAs GaP
strained strained

Gav

ZB eq.

0.0 -1- HH 0
-.12

tioned above results in the following energies (all in eV):

for GaAs, I 3, =0 and I &,

= —0.24, while for GaP,
I 3„=—0.57 and I"„=—0.42. As in the case of the (001)
interface, the GaAs forms the quantum wells while the GaP forms the barriers. The SL valence-band-maxima states will thus be localized to the GaAs region.
We introduce spin-orbit effects using the quasicubic model described in Sec. IVB. The resulting levels of the strained GaP and GaAs are shown in Fig. 13. To-gether with these calculated valence-band offsets shown are conduction-band offsets obtained by shifting the cal-culated conduction-band levels by a state-dependent gap correction that is the same as that needed to fix the calcu-lated zinc-blende equilibrium levels to their experimental values. The resulting offsets are very similar to their values for the (001) SL: the valence-band off'set is 0.52 eV
between

valence-band Td (resu863.56 5510.58 Tf6 Tf 20

localized a

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These.56 BT /Xi18 108.45T BT385 683.11 1 Tfcan.56 BT /Xi18 108.3ET BT401144T683.11 1 Tfbe.56 BT /Xi18 108.0ET BT413.78 683.Xi1f Tfinclu

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X=
g

X

+ Limni =X +L

+

j=

—n+1

(16)

Figure 15 shows the (111)dispersion of the VCA bands between the main band-edge valleys. Figure 15(a) shows the states that are folded to

I in the SL, while Fig. 15(b)
shows the VCA states folded to X. From the analysis of Sec. III, the following general observations can be made simply from these VCA band plots. First, consider the top valence bands in Fig. 15. They both show only one valley being involved (the VCA

I for I, and the VCA
L

&

&

&

for

X), and are thus expected to give rise only to standard Kronig-Penney-type SL states. The

1 -L

&

&

&

dispersion of about

1 eV is only one-third of the (001) I-
X' dispersion shown in Fig. 2(a). We thus expect the (111)

I valence-band-edge states to localize in their GaAs
well much faster than they did for (001), due to the heavier mass now involved. Consideration of the conduc-tion bands in Fig. 15, however, suggests that there might be strong intervalley mixing both at

I and at X, due to
the nearness in energy of all three of the main VCA conduction-band valleys. We thus do not expect to see
there the typical Kronig-Penney-type behavior that is ex-
pected in the SL valence-band-edge states.
Figures 16 and 17 show the SL states at

I and at X, to-
gether wif 272.67 511 Td (mig4248.tates.)Tj ET B2 469.791w BT 6T BT /X 448.4n

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2.4—

2.2-

n=t

z

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SL then yields the following result: the three main band

edges of the parent zinc-blende compound (I, X, and L)
are folded to four points in the SL zone. The resulting
folding relationships, shown in Fig. 18, are

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GaAso5 PO5 VGA bands for [201] on a»b = a

(a) [201] 1-X, -. (b) [201] X„-X„ (c)[201]L«,-L«-,

—XZ XzX, X„
[201] Direction

Xy L111

FICx.

FICx.

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1)

0
l~

(a) (001) (GaAs)2 (GaP)2

-2 I I I
Ga As Ga As Ga P Ga P Ga

0.6

{b}{111}(GaAs)2 (AIAs)2 —0 0.3—

Q)

-0.3—

U~U

-0.6

I

GaAs GaAs

I I

Al As Al As

FIG. 20. Superlattice ordering potential 6V for the (001)

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and

(X;,iSViX;,) =0. (B2)

Class X operations X~ operations

TABLE VI. Realizations of the point group D,d as the point
group of k at X" and X~ in the zinc-blende Brillouin zone.

2. (001)superlattice levels at M

In this section we derive the selection rules governing the band-edge states at the M point in the (001) SL zone. The conduction-band edge at M is determined from the
4X4 Hamiltonian matrix (X&,&~3, ~5V~xf, &~3,), and it is
our present purpose to determine which of these matrix elements are forced to vanish by symmetry. As noted above, if the coordinate origin is fixed on a central anion for odd n and on a central cation for even n, 6V has the full symmetry of the point group D2d shown in Table V. Furthermore, the VCA basis states X„and X3~ also have D2d as their point group of k, their particular realizations of this group being given in Table VI, and their transfor-mation properties under these operations being given in Table V. The first selection rule we derive is that

(x, svx, &=0, (B3)

this holding regardless of the x or y origin of either of the X& or X3 states involved. Note that the operation C2, is common to the 2C2 class of all three realizations of D2d given in Tables V and VI. Equation (B3) then follows simply by noting that 5V and any X, state are even under C2„while any X3 state is odd under it. The second selec-tion rule we derive is that

(B4)

This follows simply by noting that 5V and X3 are even under Cz, while X~3 is odd under it. (Notice that Cz, be-longs to different classes in the X and X» realizations of D2d given in Table VI.) These two selection rules result

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2028 (1989); Phys. Rev. B 39, 1871 (1989}; R. Resta, L.
Columbo, and S. Baroni, ibid. 41, 12 358 (1990).
J. Tersoff, in Heterojunction Band Discontinuities: Physics and
Device Applications, edited by F. Capasso and G. Margariton-
do (North-Holland, Amsterdam, 1987), p. 3.
T. Nakayama and H. Kamimura, J. Phys. Soc. Jpn. 54, 4726 (1985).
These energies differ slightly from the results (1.97 and 2.83

eV) of a previous calculation [S.-H. Wei and A. Zunger, Appl. Phys. Lett. 53, 2077 l1988)] due to the weighted average gap correction performed there.
S.-H. Wei and A. Zunger, Phys. Rev. B 39, 3279 (1989).
S. Baroni, R. Resta, and A. Baldereschi, in Band