



Dependence of the optical properties of semiconductor alloys on the degree of long range order

Gi <i U]K Y]ž8Uj]X'6"@U_gžUbX'5'YI 'Ni b[Yf'

7]U]h]cb. '5dd']YX'D\ng]M]g '@YH]fg' 62ž%' + 'f] - ' Ł/Xc]. '%"\$%\$*' #%'\$- (- *

J]Yk 'cb]bY. '\hd. ##Xl "Xc]"cf[#%'\$%\$*' #%'\$- (- *

J]Yk 'HUVY'cZ7 cb]Yb]g. '\hd. #g]V]U]h]cb"U]d"cf[#%'\$%\$%\$* #%'\$%\$%\$* 3j Yf1 dXZ]V]

Di V]g\YX'Vmi]Y'5=Đ Di V]g\]b[

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; fck Ĥ 'Y'a dYfU]i fY'XYdYbXYbVW'cZ'cb[fUb[Y'U`cmcfXYf'UbX'a U[bY]WdfcdYf]Yg'cZYd]fU]]U': Y'I 'Df% I fl '\$) ŁZ]a g'

5dd""D\ng]"@YH]'69ž%'* 'f] - * Ł/%"\$%\$*' #%'\$%\$*' , ' .

C d]h]W]'gdYV]f]cgV]d]WcVgYfj U]h]cb'cZgdc]b]U]b]Yci g'cb['fUb[Y'cfXYf]b[]b'5'; U=Đ

5dd""D\ng]"@YH]'68ž' &* 'f] - * Ł/%"\$%\$*' #%'\$%\$%\$*) * - .

@cb[fUb[Y'Q%Qc'fXYf]b[]b'; U5g% I 'D' I'

5dd""D\ng]"@YH]'54ž% - \$'f] - , - Ł/%"\$%\$*' #%'\$%\$%&' &'

@cb[fUb[Y'cfXYf]b[]b'5gGV'

5dd""D\ng]"@YH]'54ž%' ('f] - , - Ł/%"\$%\$*' #%'\$%\$%\$+(* - .

C fXYf]b[]bXi WX'WUb[Yg]b'ĤY'cd]h]W]'gdYV]f]U'cZgYa]V]bXi V]cf'U`cng'

5dd""D\ng]"@YH]'52ž' %&'f] - , Ł/%"\$%\$*' #%'\$-) \$' .

Dependence of the optical properties of semiconductor alloys on the degree of long-range order

Su-Huai Wei, David B. Laks, and Alex Zunger
National Renewable Energy Laboratory, Golden, Colorado 80401

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Many III-V semiconductor alloys exhibit metastable [111] structures grown from the vapor phase. This is manifested by the splitting of the valence-band maximum and by a reduction in the direct band gap. We show here how these features can be used to deduce quantitatively the degree of long-range order in a given sample. Examples are given for $\text{Ga}_{0.5}\text{In}_{0.5}\text{P}$ and $\text{Ga}_{0.5}\text{In}_{0.5}\text{As}$ alloys.

Bulk semiconductor alloys grown at high temperatures are nearly perfectly random.¹ On the other hand, low temperature growth, especially of a size mismatched alloy such as $\text{Ga}_{0.5}\text{In}_{0.5}\text{P}$ or $\text{Ga}_{0.5}\text{In}_{0.5}\text{As}$, is manifested by a preferential association of like atoms ("clustering") or unlike atoms ("anticlustering") and is seen in diffuse scattering,² Raman³ infrared⁴ and nuclear magnetic resonance chemical

further manifested by the appearance of superlattice diffraction (VBM) degeneracy,^{5,6} and altered polarizations⁷ evident in optical experiment. The present theoretical understanding of perfectly random semiconductor alloys (e.g., $\text{Al}_x\text{Ga}_{1-x}\text{As}$) and of perfectly ordered compoundlike structures [e.g., short-period $(\text{AlAs})_n(\text{GaAs})_m$ superlattices] is rather advanced. However, many semiconductor alloys exhibit partial LRO for which theoretical descriptions

in vapor-phase growth of virtually all III-V alloys⁶ is an example of the imperfect ordering: successive atomic layers along [111] are not pure A or pure B. The degree of ordering depends on growth temperature, growth rates, III/V ratio, substrate misorientation, and doping. Electron diffraction does not provide a quantitative measure of LRO, and current theories do not relate the optical properties to the degree of LRO. We introduce here a general

alloys with partial LRO in terms of the properties of (i) the perfectly random alloy (LRO parameter $\eta=0$) and (ii) the perfectly ordered structure (LRO parameter $\eta=1$). We use optical data. We find that for most metalorganic-chemical-vapor-deposition-grown $\text{Ga}_{0.5}\text{In}_{0.5}\text{P}$ and $\text{Ga}_{0.5}\text{In}_{0.5}\text{As}$ systems, we also provide predictions for the $\text{Ga}_{0.5}\text{In}_{0.5}\text{As}$ system.

Our approach is based on a statistical description of substitutional A_{1-x}B_x system in terms of Ising model.¹¹ A configuration σ is defined as a particular occupation of each of the N lattice sites by either an A or a B atom. If site i is occupied by A we label it by the spin variable $\hat{S}_i = -1$,

when it is occupied by B we have $\hat{S}_i = +1$. The lattice is further broken into "figures," each consisting of a grouping of k sites ($k=1, 2, 3, \dots$ corresponds to single sites, pairs, and triplets, etc.). The average spin products for all figures f in a class F

$$\bar{S}_F(\sigma) = \frac{1}{N} \sum_{\sigma} \hat{S}_1(\sigma) \hat{S}_2(\sigma) \dots \hat{S}_k(\sigma) \quad (1)$$

where σ is a configuration of spins, $\hat{S}_i(\sigma)$ is the spin variable of site i in configuration σ , and N is the total number of configurations. $\{\Pi_F(\sigma)\}$ forms an orthonormal basis; consequently, any lattice property $P(\sigma)$ (e.g., total energy, band gap) can be expanded rigorously as

$$P(\sigma) = N \sum_F D_F P_F \Pi_F(\sigma), \quad (2)$$

where $D_F = \langle \Pi_F | P | \Pi_F \rangle$ and P_F is the contribution of figure F to

tween widely separated atoms, or between many atoms interacting simultaneously, are less important than those between nearby pairs of atoms. In this case, it is possible to calculate the contribution p_F of the dominant interactions from electronic structure studies of a small set of ordered configurations.^{11,12} This set of p_F can then be used in Eq. (2) to predict the property $P(\sigma)$ of any of the 2^N ordered configurations. This has been widely applied to study the

respect to a particular ordered structure σ whose composition is X_A . For example, the ordered CuPt structure has $X_A = 1/2$ and consists of two sublattices, one occupied by A and the other by B. In the CuPt structure the A sublattice is occupied in part also by B and vice versa. To study such systems we replace the discrete spin variables \hat{S}_i by continuous variables $\hat{S}_i(x, \eta)$ which is

$$\langle \hat{S}_i(x, \eta) \rangle = (2x - 1) + \eta \sum_{k \neq 0} \hat{S}(\mathbf{k}, \sigma) e^{i\mathbf{k} \cdot \mathbf{R}_i} \quad (3)$$

Here $\hat{S}(\mathbf{k}, \sigma)$ is the Fourier transform of the spin variables of the perfectly ordered structure σ and the sum runs over

the points in the Brillouin zone. Applying Eq. (2) to the

To compute the properties (P) of the alloy at any η value, we first obtain the correlation functions of Eq. (1) using Eq. (4), and then insert these into the Ising model.² This

To illustrate this general method, imagine a giant supercell of size n lattice constants along the z axis. At a given η value, according to Eq. (3). Treat this supercell as an "ordinary" crystal with periodic boundary condition. The total energy can be calculated using, e.g., the valence force field (VFF)¹⁴ method. This direct approach will produce statistically accurate results for P vs η if sufficient sites are

simpler approximation will be tested. The latter can be used if the pair interactions are dominant. Using Eqs. (1) and (4) one has for F -pair figures

Using Eq. (2), Eq. (5) implies that for property P ,

$$P(x, \eta) = P(x, 0) + \eta^2 [P(x, 1) - P(x, 0)] \quad (6)$$

of coordinates. This equation relates the property P at any degree of LRO to the corresponding properties in (i) the perfectly random alloy at compositions x and X_σ and (ii) the perfectly ordered structure at composition X . Note that Eq. (6) neglects SKO beyond that implied by the assumed LRO.

We first examine the accuracy of Eq. (6) by performing *direct calculations* of a $\text{Ga}_{0.5}\text{In}_{0.5}\text{P}$ alloy with CuPt LRO. Such a calculation is not limited to pair interactions. A giant, 2048 atom supercell is occupied by Ga and In atoms according to Eq. (3) (the phosphorus atoms always reside at their own sublattice). The total elastic energy of such a configuration is minimized by permitting all atoms

The average elastic energy at $\eta = 1/4, 1/2$, and $3/4$ are 21.0, 23.2, and 26.6 meV/atom, respectively. These can be compared with the values predicted by the simple expression (6): 20.9, 22.9, and 26.3 meV/atom, respectively, in excellent agreement with the direct supercell calculations.

Having established the accuracy of Eq. (6) we now apply it to study the optical properties of semiconductor alloys as a function of the degree of CuPt LRO. Wei and co-workers¹⁵ have shown that the optical absorption of GaAs can be described fairly well by the quasicubic model¹⁶ as

the degree of LRO. The total energy of the supercell is minimized by permitting all atoms to relax. The results are summarized in Table I. Note that in addition to cell-internal distortion (e.g., the relaxation of the P atoms), the interface coherence is removed, but in the presence of coherence with a (001) substrate, this distortion can be inhibited, resulting in a cubic or tetragonal film. Table I gives Δ_0 and Δ_{CF} for both the relaxed (rhombohedral) and unrelaxed (cubic or tetragonal) cases.

	$\text{Ga}_{0.5}\text{In}_{0.5}\text{P}$	$\text{Ga}_{0.5}\text{In}_{0.5}\text{As}$
$\Delta_0(0)$	0.100	0.35
$\Delta_0(1)$	0.105	0.35
$\Delta_{CF}(1)_{\text{rel}}$	0.31	0.18
Δ_{CF}	-0.32	-0.30

$$E_{1,2,3} = \begin{cases} \frac{1}{2} (\Delta_0 + \Delta_{CF}) \\ \pm \frac{1}{2} [(\Delta_0 + \Delta_{CF})^2 - \frac{8}{3} \Delta_0 \Delta_{CF}]^{1/2} \end{cases} \quad (7)$$

is the crystal-field splitting in the absence of spin-orbit coupling, light-hole, and spin-orbit states, respectively [Eq. (7) shows that these are, in fact, coupled]. $\Delta_0(\eta)$ and $\Delta_{CF}(\eta)$ can be calculated using Eq. (6) since the properties of the random alloy ($\eta = 0$) and 1. The values are given in Table I.

the total energy with respect to the structural parameters. The results are summarized in Table I. Note that in addition to cell-internal distortion (e.g., the relaxation of the P

or the interface coherence is removed), but in the presence of coherence with a (001) substrate, this distortion can be inhibited, resulting in a cubic or tetragonal film. Table I gives Δ_0 and Δ_{CF} for both the relaxed (rhombohedral) and unrelaxed (cubic or tetragonal) cases.

We can now calculate $E_i(\eta)$ vs η by applying Eq. (6) to $\Delta_0(\eta)$ and $\Delta_{CF}(\eta)$ in Eq. (7), using our calculated values at $\eta = 0$ and 1 of Table I. This gives $E_i(\eta)$ as a power series in η . Since no independent measurement exists to indicate whether a rhombohedral distortion exists, we present in Fig. 1 results both for the relaxed and unrelaxed cases: The solid lines are calculated for constrained alloys without rhombohedral relaxation and the dashed

random alloy ($\eta = 1$) is a pure spin-orbit state. While the lines of Fig. 1 represent nonempirical first-principles predictions, they can be used to infer the degree of LRO in a given sample from optical measurements. The open circles in Fig. 1(a) represent the polarized photoluminescence results of Kanata *et al.*⁷ for $\text{Ga}_{0.5}\text{In}_{0.5}\text{P}$, while the solid circles are the polarized electromodulation results of Glombitski *et al.*⁸ for $\text{Ga}_{0.5}\text{In}_{0.5}\text{P}$. We note that the 0.77 eV theory provides a good fit for these independent sets of data. Furthermore, the value of η deduced from the

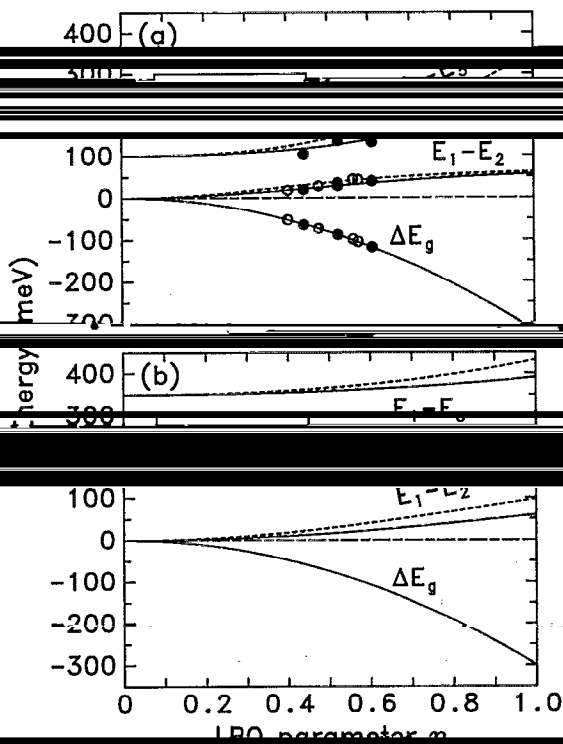


FIG. 1. Calculated valence band splitting $E_1 - E_2$ and $E_1 - E_2$ [Eq. (7)]

vs LRO parameter η for Ga_{0.51}In_{0.49}P/GaAs. The open circles in (a) are the experimental results of McDermott *et al.* (Ref. 7) for five samples grown at different temperatures, while the solid circles are the results of Glembocki *et al.* (Ref. 8) for three samples.

measured ΔE_g is consistent with the η value deduced from least-square fitting to both ΔE_g and the $E_1 - E_2$ valence-

$E_1 - E_2$ vs η line for large η distinguishes the relaxed and

et al.' postulating linearity with η . The large reduction in band gap $\Delta E_g = 0.14$ eV measured by McDermott *et al.*¹⁸

in the ALE growth of Ga_{0.51}In_{0.49}P/GaAs is probably the

This work illustrates how optical experiments can be used to deduce the degree of LRO, thus, correlating growth conditions with LRO. It would be interesting to correlate the optically deduced LRO with that measured directly in future *quantitative* diffraction experiments.

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the orbital mixing at VBM is estimated to be less than 20 meV for the

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