



# 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. #gV]U]h]cb"U]d"cf[ #Łcb]Yb]U]d#ci fbU'#Ud# &#%' 3j Yf1 dXZŁž

Di V]g\YX'Vm]h]Y'5=Đ Di V]g\]b[

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; fck h' ]Ya dYfU]i fY'XYdYbXYbW'cZ'cb[ fUb[ Y'U`cmcfXYf'UbX'a U[ bY]h]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]Łd]WcVgYfj U]h]cb'cZgdc]b]U]b]Yci g'cb[ 'fUb[ Y'cfXYf]b[ ]b'5'; U=ŁD'

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

@cb[ fUb[ Y'Ł%Ł%Ł%cfXYf]b[ ]b'; U5g% I 'D' I'

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

@cb[ fUb[ Y'cfXYf]b[ ]b'Ł5gGV'

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

C fXYf]b[ ]bXi W'X'W'Ub[ Yg]b' h]Y'cd]h]W'gdYV]U'cZgYa ]ŁbXi V]Łcf'U`cng'

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

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

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(Received 9 September 1992; accepted for publication 21 January 1993)

Many III-V semiconductor alloys exhibit metastable [111] domains 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.<sup>1</sup> On the other hand, low temperature growth, especially of a size mismatched alloy such as  $\text{Ga}_{0.5}\text{In}_{0.5}\text{P}$ , leads to metastable [111] domains. This is manifested by a preferential association of like atoms ("clustering") or unlike atoms ("anticlustering") and is seen in diffuse scattering,<sup>2</sup> Raman,<sup>3</sup> infrared,<sup>4</sup> and nuclear magnetic resonance chemical shift.<sup>5</sup> The [111] domains are further manifested by the appearance of superlattice diffraction (SLD) degeneracy<sup>6</sup> and altered polarizations<sup>7</sup> evident in x-ray scattering. The ordering 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 are lacking.

In vapor-phase growth of virtually all III-V alloys<sup>6</sup> 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 theoretical method for describing alloy properties as a function of the degree of LRO.

We describe the properties of alloys with partial LRO in terms of the properties of (i) the perfectly random alloy (LRO parameter  $\eta=0$ ) and (ii) the perfectly ordered alloy ( $\eta=1$ ). The degree of LRO is characterized by the parameter  $\eta$ , which is defined as the ratio of the average spin product to the value for a perfectly ordered alloy. We use optical data. We find that for most metalorganic-chemical-vapor-deposition-grown  $\text{Ga}_{0.5}\text{In}_{0.5}\text{P}$  alloys (e.g., Refs. 7, 8)  $\eta \sim 0.3-0.6$ . 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  $\text{A}_{1-x}\text{B}_x$  system in terms of Ising model.<sup>11</sup> A configuration  $\sigma$  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  $F$

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

can be expanded rigorously as

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

where  $D_F = \Omega_F / N$  and  $p_F$  is the contribution of figure  $F$  to the property  $P(\sigma)$ .

Interactions between 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.<sup>11,12</sup> 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 ordered configurations of many binary systems.<sup>11,12</sup>

respect to a particular ordered structure  $\sigma$  whose composition is  $X_B$ . For example, the ordered CuPt structure has  $X_B = 1/2$  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  $\hat{S}_i = \pm 1$  by the ensemble average value, which is

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

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

the points in the Brillouin zone. Applying Eq. (2) to the  $F$  then gives<sup>13</sup>

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

To illustrate this general method, imagine a giant supercell whose sites are occupied by A or B atoms, for given  $\eta$  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)<sup>14</sup> method. This direct approach will produce statistically accurate results for  $P$  vs  $\eta$  if sufficient sites are

simpler approximation will be tested. The latter can be 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  $X_\sigma$  and (ii) the perfectly ordered structure at composition  $X_\sigma$ . Note that Eq. (6) neglects SRO 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 to relax using the VFF model.<sup>14</sup> To obtain  $P$  vs  $\eta$

The average elastic energy at  $\eta = 0, 1/2$ , and  $1$  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 *et al.* have shown that the optical absorption and emission energies can be described fairly well by the quasicubic model<sup>16</sup> as

phases, and band-gap reduction ( $\Delta E_g$ ) of the ordered phase relative to the random alloy. Results (in eV) are given for two alloys. For  $\Delta_{\text{CF}}(1)$  we give results calculated with and without rhombohedral relaxation. The  $\Delta_0$

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

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

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  $\Delta_{\text{CF}}(\eta)$  can be calculated using Eq. (6) since the values at  $\eta = 0$  and  $1$  are known. The  $\Delta_0$  and  $\Delta_{\text{CF}}$  are

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  $\Delta_{\text{CF}}(1)$  for both the relaxed (rhombohedral) and unrelaxed (cubic or tetragonal) cases.

We can now calculate  $E_i(\eta)$  vs  $\eta$  by applying Eq. (6) to  $\Delta_0(\eta)$  and  $\Delta_{\text{CF}}(\eta)$  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  $\eta$ . 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 lines are calculated for the fully relaxed alloys. Note that the random alloy ( $\eta = 0$ ) 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.*<sup>7</sup> for  $\text{Ga}_{0.5}\text{In}_{0.5}\text{P}$ , while the solid circles are the polarized electromodulation results of Glendon *et al.*<sup>18</sup> for  $\text{Ga}_{0.5}\text{In}_{0.5}\text{P}$ . We note that the theory provides a good fit for these independent sets of data. Furthermore, the value of  $\eta$  deduced from the

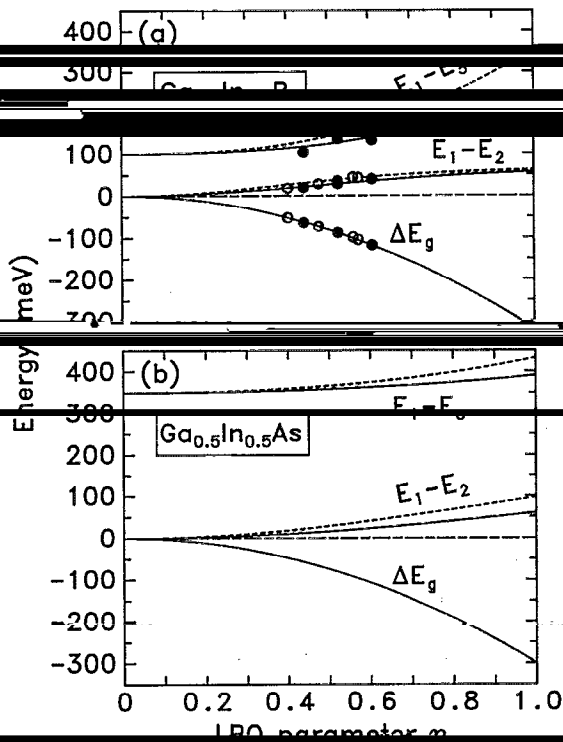


FIG. 1. Calculated valence band splitting  $E_1 - E_2$  and  $E_1 - E_0$  [Eq. (7)]

vs LRO parameter  $\eta$  for  $\text{Ga}_{0.5}\text{In}_{0.5}\text{P}$  (a) and  $\text{Ga}_{0.5}\text{In}_{0.5}\text{As}$  (b). The open circles in (a) are the experimental data from Glembocki 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  $\Delta E_g$  is consistent with the  $\eta$  value deduced from least-square fitting to both  $\Delta E_g$  and the  $E_1 - E_0$  valence-

$E_1 - E_0$  vs  $\eta$  line for large  $\eta$  distinguishes the relaxed and

et al.' postulating linearity with  $\eta$ . The large reduction in band gap  $\Delta E_g = 0.14$  eV measured by McDermott et al.<sup>18</sup>

in the ALE growth of  $\text{Ga}_{0.51}\text{In}_{0.49}\text{P}/\text{GaAs}$  is probably the result of the strain-induced LRO in this system. Figure 1(b) provides predictions for the yet

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.

This work was supported in part by the U.S. Depart-

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<sup>13</sup>The degree of LRO is limited by the requirement that  $|\langle \hat{S}_i(x, \eta) \rangle| < 1$ , which by use of Eq. (4) implies that  $0 < \eta < \min[x/X_m(1-x)/(1-X_m)]$ . Perfect ordering ( $\eta = 1$ ) is possible only when  $x = X_m$ .

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

D. C. 15. A similar analysis requires a more accurate treat-

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