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

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

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[redacted] 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 $Ga_{0.5}In_{0.5}P$ and $Ga_{0.5}In_{0.5}As$ alloys.

Bulk semiconductor alloys grown at high temperatures are nearly perfectly random.[1] On the other hand, low tem- [redacted] sociation of like atoms ("clustering") or unlike atoms ("anticlustering") and is seen in diffuse scattering,[2] Ra- [redacted] (VBM) degeneracy,[7,8] and altered polarizations[9] evident in optical experiment. The present theoretical understanding of perfectly random semiconductor alloys (e.g., [redacted] tices] is rather advanced. However, many semiconductor [redacted] in vapor-phase growth of virtually all III-V alloys[6] 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 [redacted] alloys with partial LRO in terms of the properties of (i) the perfectly random alloy (LRO parameter $\eta=0$) and [redacted] optical data. We find that for most metalorganic-chemical- [redacted] $Ga_{0.5}In_{0.5}As$ 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 [redacted] erage spin products for all figures f in a class F

[redacted]

$\{\Pi_F(\sigma)\}$ forms an orthonormal basis; consequently, any lattice property $P(\sigma)$ (e.g., total energy, band gap) can be expanded rigorously as

[redacted]

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 [redacted] respect to a particular ordered structure σ whose composition is X_σ. For example, the ordered CuPt structure has [redacted] which is

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

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

[redacted]

To compute the properties $\langle P\rangle$ 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 [redacted]

To illustrate this general method, imagine a giant su- [redacted] 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 [redacted] simpler approximation will be tested. The latter can be [redacted] the pair interactions are dominant. Using Eqs. (1) and (4) one has for F=pair figures

[redacted]

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

[redacted] 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) [redacted] 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 $Ga_{0.5}In_{0.5}P$ 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 [redacted] 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 [redacted] can be described fairly well by the quasicubic model[16] as

[redacted]

	$Ga_{0.5}In_{0.5}P$	$Ga_{0.5}In_{0.5}As$
$\Delta_0(0)$	0.100	0.35
$\Delta_0(1)$	0.105	0.35
[redacted]	[redacted]	[redacted]
$\Delta_{CF}(1)_{rel}$	0.31	0.18
[redacted]	[redacted]	[redacted]

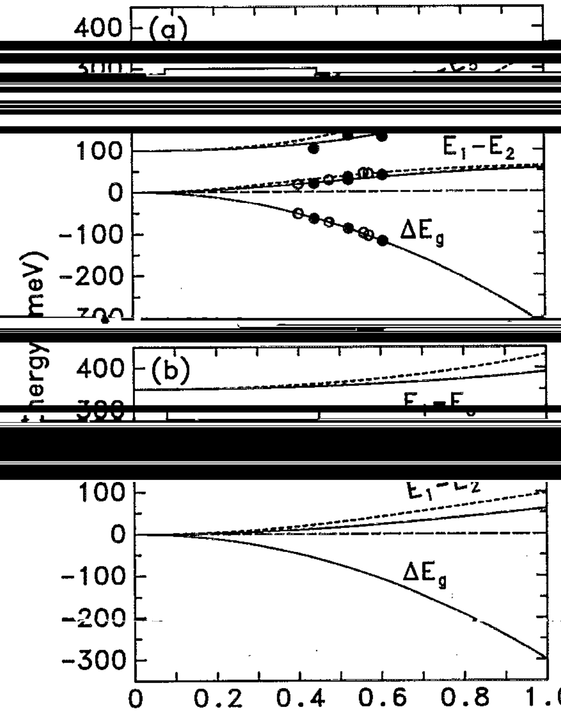
$$E_{1,2,3}=\begin{cases}\frac{1}{2}(\Delta_0+\Delta_{CF})\\ \pm\frac{1}{2}[(\Delta_0+\Delta_{CF})^2-\frac{8}{3}\Delta_0\Delta_{CF}]^{1/2},\end{cases}\qquad(7)$$

[redacted] is the crystal-field splitting in the absence of spin-orbit cou- [redacted] shows that these are, in fact, coupled]. $\Delta_0(\eta)$ and $\Delta_{CF}(\eta)$ [redacted] 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 [redacted] 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 [redacted] 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 [redacted]

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 $Ga_{0.5}In_{0.5}P$, while the solid circles are the polarized electromodulation results [redacted] sets of data. Furthermore, the value of η deduced from the

[redacted]



[redacted]

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 [redacted] E_1-E_2 vs η line for large η distinguishes the relaxed and [redacted] *et al.*[7] 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 [redacted]

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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[redacted]

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

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