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Many III-V semiconductor alloys exhibit spontaneous [111] alternate monolayer ordering when 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 temperature growth, especially of a size-mismatched alloy such as GaInP leads to deviations from randomness that show either as short-range (SRO) order[2–5] or long-range order (LRO).[6–10] SRO is manifested by a preferential association of like atoms ("clustering") or unlike atoms ("anticlustering") and is seen in diffuse scattering,[2] Raman,[3] infrared,[4] and nuclear magnetic resonance chemical shift.[5] LRO, which is the subject of the present letter, is further manifested by the appearance of superlattice diffraction spots,[6] removal of valence-band maximum (VBM) degeneracy,[7,8] and altered polarizations[9] evident in optical experiment. The present theoretical understanding of perfectly random semiconductor alloys (e.g., $Al_{1-x}Ga_xAs$) and of perfectly ordered compoundlike structures [e.g., short-period $(AlAs)_n/(GaAs)_m$ superlattices] is rather advanced. However, many semiconductor alloys exhibit *partial* LRO for which theoretical description is lacking. The spontaneous monolayer A/B alternation along the [111] direction ("CuPt ordering") observed 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 theoretical method for describing alloy properties as a function of the degree of LRO. We derive from this general theory a simplified formula that describes 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 ordered superlattice ($\eta=1$). This permits the deduction of the degree of ordering from the analysis of the optical data. We find that for most metalorganic-chemical-vapor-deposition-grown $Ga_{0.5}In_{0.5}P$ alloys (e.g., Refs. 7, 8) $\eta \sim 0.3$–0.6. We also provide predictions for the $Ga_{0.5}In_{0.5}As$ 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 k sites ($k=1$, 2, 3 corresponds to single sites, pairs, and triangles, etc.). It is possible to characterize a given atomic configuration σ by the collection of its "correlation function" $\bar{\Pi}_F(\sigma)$ for the prototype figure F. These are the average spin products for all figures f in a class F

$$\bar{\Pi}_F(\sigma) = 1/O_F \sum_f \hat{S}_{i_1}(\sigma)\hat{S}_{i_2}(\sigma)\cdots\hat{S}_{i_k}(\sigma), \quad (1)$$

where f runs over the O_F figures of class F, and the spin product is taken over the k vertices of a figure f. The set $\{\bar{\Pi}_F(\sigma)\}$ forms an orthonormal basis; consequently, any lattice property $P(\sigma)$ (e.g., total energy, band gap) can be expanded rigorously as

$$P(\sigma) = N \sum_F D_F p_F \bar{\Pi}_F(\sigma), \quad (2)$$

where $D_F = O_F/N$ and p_F is the contribution of figure F to the property P. Calculations[11,12] have shown that often there is a hierarchy of figures, i.e., that 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.[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 *ordered configurations* of many binary systems.[11,12]

This approach can be generalized now to *partially* ordered structures. The degree η of LRO is defined with respect to a particular ordered structure σ whose composition is X_σ. For example, the ordered CuPt structure has $X_\sigma=1/2$ and consists of two sublattices: one occupied by A and the other occupied by B. In the *partially* ordered 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

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

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. (3) to the perfectly ordered structure ($\eta=1$) with composition X_σ then gives[13]

$$\langle \hat{S}_i(x,\eta) \rangle = (2x-1) + \eta[\hat{S}_i(\sigma) - (2X_\sigma-1)]. \quad (4)$$

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 provides a general Ising expansion for any lattice property P at an arbitrary η.

To illustrate this general method, imagine a giant supercell whose sites are occupied by A or B atoms, for 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 included. We will illustrate this (in principle exact) approach below to establish a benchmark against which a simpler approximation will be tested. The latter can be constructed by noticing that in many practical situations the pair interactions are dominant. Using Eqs. (1) and (4) one has for $F=$ pair figures

$$\bar{\Pi}_F(x,\eta) = (2x-1)^2 + \eta^2[\bar{\Pi}_F(\sigma) - (2X_\sigma-1)^2]. \quad (5)$$

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

$$P(x,\eta) = P(x,0) + \eta^2[P(X_\sigma,1) - P(X_\sigma,01)], \quad (6)$$

provided that the property can be well expressed in terms of single site and pair interactions and that the lattice property is independent of the choice of the origin of the system 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_σ. 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 $Ga_{0.5}In_{0.5}P$ 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 to relax, using the VFF model.[14] To obtain a configurational average, this is repeated 20 times for each η value. The average "exact" 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 Zunger[15] have shown that the VBM of the random alloy is split by the CuPt ordering into three levels. Their energies can be described fairly well by the quasicubic model[16] as

TABLE I. Calculated spin-orbit splitting (Δ_0) and crystal-field splitting (Δ_{CF}) for the perfectly ordered ($\eta=1$) and perfectly random ($\eta=0$) phases, and band-gap reduction (ΔE_g) of the ordered phase relative to the random alloy. Results (in eV) are given for two alloys. For $\Delta_{CF}(1)$ we give results calculated with and without rhombohedral relaxation. The Δ_0 and ΔE_g values are rather insensitive to the rhombohedral distortion.

	$Ga_{0.5}In_{0.5}P$	$Ga_{0.5}In_{0.5}As$
$\Delta_0(0)$	0.100	0.35
$\Delta_0(1)$	0.105	0.35
$\Delta_{CF}(0)$	0.0	0.0
$\Delta_{CF}(1)_{unrel}$	0.20	0.10
$\Delta_{CF}(1)_{rel}$	0.31	0.18
ΔE_g	−0.32	−0.30

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

where Δ_0 is the spin-orbit splitting in a cubic field and Δ_{CF} is the crystal-field splitting in the absence of spin-orbit coupling. Loosely speaking, levels $|1\rangle$, $|2\rangle$, and $|3\rangle$ are heavy-hole, light-hole, and split-off states, respectively [Eq. (7) shows that these are, in fact, coupled]. $\Delta_0(\eta)$ and $\Delta_{CF}(\eta)$ can be calculated using Eq. (6) given the values at the end points $\eta=0$ and 1. The latter are obtained from self-consistent band-structure calculations[15,17] after minimizing 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 atom in $Ga_{0.5}In_{0.5}P$), an ordered CuPt structure could have a rhombohedral distortion along the [111] superlattice ordering direction. This should always occur in a "free-floating" sample (e.g., when the substrate is removed 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 $\Delta_{CF}(1)$ 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 lines are calculated for the fully relaxed alloys. Note that at $\eta=0$ we have $E_1-E_3=\Delta_0$ and $E_1-E_2=0$, so only in the random alloy $|3\rangle$ is a pure split-off 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 $Ga_{0.5}In_{0.5}P$, while the solid circles are the polarized electromodulation results of Glembocki et al.[8] for $Ga_{0.52}In_{0.48}P$. We assume that the room-temperature random alloy band gap $E_g(0)=1.910$ eV. Our theory provides a good fit for these independent sets of data. Furthermore, the value of η deduced from the
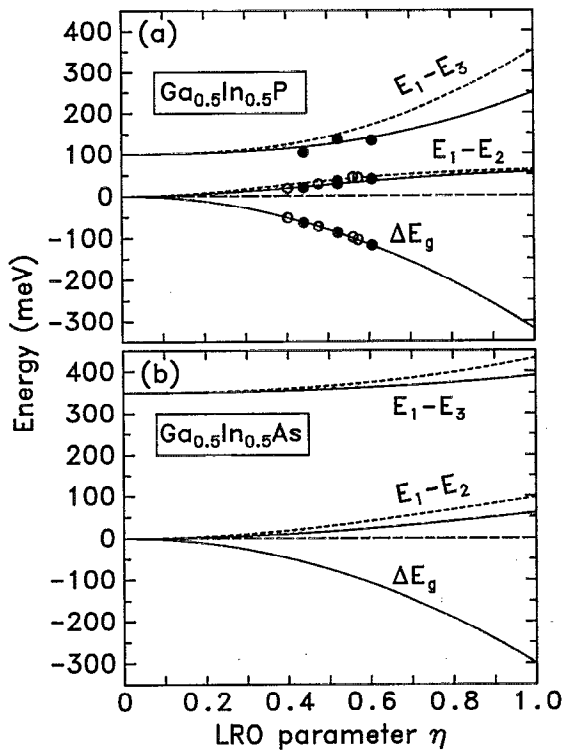
FIG. 1. Calculated valence-band splitting E_1-E_2 and E_1-E_3 [Eq. (7)] and band-gap reduction energies ΔE_g as function of CuPt LRO parameter η for (a) $Ga_{0.5}In_{0.5}P$ and (b) $Ga_{0.5}In_{0.5}As$. Solid lines are calculated using unrelaxed $\Delta_{CF}(\eta=1)$ while dashed lines are calculated using relaxed $\Delta_{CF}(\eta=1)$. The open circles in (a) are the experimental data of Kanata 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-band splitting. The derived ordering parameters are insensitive (to within 2%) to the values of $\Delta_{CF}(\eta=1)$, yet the E_1-E_3 vs η line for large η distinguishes the relaxed and unrelaxed cases. Note that the degree of LRO deduced from the correct quadratic formula [Eq. (6)] is significantly larger than that deduced incorrectly by Kanata 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 largest degree of ordering ($\eta=0.66$) observed so far for this system. Figure 1(b) provides predictions for the yet unmeasured $Ga_{0.5}In_{0.5}As$ system.

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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