Effects of atomic clustering on the optical properties of III-V alloys

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Self-consistent electronic structure calculations together with a structural model are used to study the effect of short-range atomic order on the optical properties of otherwise random $Al_{0.5}Ga_{0.5}As$, $Ga_{0.5}In_{0.5}P$, and $Al_{0.5}In_{0.5}As$ alloys. We find that clustering can reduce the direct band gap of these alloys by as much as 100 meV. Furthermore, sufficiently strong clustering is predicted to transform $Al_{0.5}Ga_{0.5}As$ into a direct gap material.

A and B atoms on their fcc sublattice. These deviations take the form of long-range order (LRO), short-range order (SRO), or both. LRO in III-V alloys appears most frequently in the CuPt structure and is accompanied by a reduction in the band gap relative to the disordered phase.[1] This gap reduction reflects zone-folding and level-repulsion[2] and de-

Warren-Cowley[4] parameter

$$\alpha_j = 1 - \frac{P_B(j)}{x_B}, \tag{1}$$

random alloy $P_B(j) = x_B$ and thus $\alpha_j = 0$ for all atomic shells.

x-ray scattering,[5,6] transmission electron microscopy,[7] and scanning tunneling microscopy.[8] Indirect evidence for SRO comes from nuclear magnetic resonance,[9] resonant Raman

experiments[5–8,11,13] report clustering-type SRO ($\alpha > 0$), whereas anticlustering seems to be less frequently

tered ($\alpha > 0$) models of $Al_{0.5}Ga_{0.5}As$, $Ga_{0.5}In_{0.5}P$, and $Al_{0.5}In_{0.5}As$ alloys. We find that local clustering can (i) reduce the band gap of III-V alloys to a similar extent as LRO does, (ii) transform the indirect-gap material $Al_{0.5}Ga_{0.5}As$ into a direct-gap one, and (iii) localizes the band edge wave functions preferentially on a particular type of cluster, which thus acts as a "local quantum-well." We will discuss the chemical trends for wave-function localization in the sequence Al/Ga/In.

The standard approach to the electronic structure of alloys—the virtual crystal approximation—does not distinguish A from B atoms irrespective of their chemical disparity. The single-site coherent potential approximation assumes

environments. A more realistic description would allow for a *distribution* of A and B atoms reflecting the existence of many distinct local atomic environments in the alloy. The most direct approach to this description would involve application of band theory to fictitious solids with huge (≥ 1000 atom) supercells[16–18] whose sites are occupied by A and B

cal tight-binding[17] and empirical pseudopotentials in a plane-wave basis.[18] These studies showed that the results can be mimicked very well using much smaller unit cells (~ 10 atoms) but with *specially selected site occupations and cell geometries* ("special quasirandom structures," or SQS).

SQSs in the context of self-consistent nonlocal pseudopoten-

(LDA) to obtain the electronic energy bands of III-V alloys

type in which the nearest-neighbor shell has $\alpha_1 > 0$ and all subsequent shells are random. We use 16-atom SQSs with the same computational parameters as described in Ref. 15. The atomic positions of $Ga_{0.5}In_{0.5}P$ and $Al_{0.5}In_{0.5}As$ in the

field,[20] while maintaining cubic symmetry for the cell-external degrees of freedom. We are interested in calculating alloy band gaps of a particular zinc-blende representation

of a few SQS states $|j\bar{K}\rangle$, weighted with the spectral density

$$\langle E_n(\mathbf{k})\rangle_{\text{alloy}} = \frac{1}{W} \sum_{j,\bar{K}} |\langle j\bar{K}|n\mathbf{k}\rangle|^2 E_j(\bar{K}), \tag{2}$$

where the sum runs over a few SQS states around a peak in the spectral density of the state $|n\mathbf{k}\rangle$, $\bar{K}$ must differ from $\mathbf{k}$ by a reciprocal lattice vector of the SQS, and W is a normalization constant.

Table I summarizes our calculated [Eq. (2)] alloy band gaps[21] with and without SRO. We choose in this study a relatively large and positive SRO parameter of $\alpha = \frac{1}{6}$ in order to emphasize the effect of local clustering. (Note, however,

randomness ($\alpha=\eta=0$), clustering-type SRO ($\alpha=\frac{1}{6}$), and CuPt-type LRO ($\eta=1$). Here, $\bar{E}_g$ denotes the average gap of the binaries at their equilibrium volumes. Chemical symbols in parentheses denote the sublattice on which

System	$\bar{E}_g$	Random	SRO $\alpha=\frac{1}{6}$	LRO $\eta=1$
X	2.18	2.17	2.16	2.10

lar type of cation tetrahedron A_nB_{4-n}. We define a cluster weight as

$$w_n(j\bar{K}) = \frac{1}{N}\sum |\langle\chi_\Omega(\mathbf{r}_i)|j\bar{K}\rangle|^2, \qquad (3)$$

where N_n is the number of clusters of type A_nB_{4-n}, the sum runs over all positions of A, B, and C atoms participating in

$Ga_{0.5}In_{0.5}P$, and the valence band maximum of $Al_{0.5}In_{0.5}As$ are also shown in Fig. 1, demonstrating localization on particular "pure" clusters. (The CBM in $Al_{0.5}In_{0.5}As$ is weakly localized on In-rich clusters.)

The results of Fig. 1 imply that the clusters act as "impurity-like traps" for electrons or holes, very much like isoelectronic impurities which are known to bind carriers if

that SRO parameters as large as the present one have been reported in the literature[5].) The table also gives the average band gaps of the binaries $\bar{E}_g=\frac{1}{2}[E_g(AC)+E_g(BC)]$ and the calculated gaps of CuPt ordered alloys ($\eta=1$). The

tive to $\bar{E}_g$ by 0.05, 0.10, and 0.13 eV for $Al_{0.5}Ga_{0.5}As$, Ga In P and Al In As respectively. This gives bowing parameters of 0.20, 0.40, and 0.52 eV, compared with the experimental results of 0.37 (Ref. 22), 0.70 (Ref. 23), and 0.74 eV (Ref. 24), respectively. (ii) LRO of the CuPt type ($\eta=1$) reduces the band gaps relative to $\bar{E}_g$ by 0.41, 0.50

parameter $\alpha=\frac{1}{6}$ also reduces significantly the direct band

direct band gap crossover in $Al_{0.5}Ga_{0.5}As$ with sufficient local clustering. This is in marked contrast to the findings of Fu et al. who find negative optical bowing upon clustering. Magri et al. obtain the same sign of band gap modifications

parameter assumed there.[15]

In order to understand the physical mechanism leading to the large gap reduction reported in Table I, we analyze the wave functions of the lowest conduction (CBM) and highest

either the lowest conduction band edge ($Al_{0.5}Ga_{0.5}As$) or the

strongly localize on clusters of one type of cations, while the corresponding states in the random alloys show no such tendency. This is illustrated by plotting contours of the wave functions squared in crystallographic planes intersecting these clusters (see right-hand side of Fig. 1). The wave func-

segregation (i.e., localization) can be quantified by projecting the wave functions on atomic spheres belonging to a particu-

we show contour plots of the corresponding wave function squared on the (110) plane. The states are clearly segregated on one type of cluster.

perturbing potential, thus enhancing its strength and leading to binding. Similarly, an isolated In impurity in GaP or AlAs will probably not bind a hole, but the corresponding clusters do. For sufficiently large cluster sizes we can rephrase the preceding argument in terms of band theory: The segregation of the band edge wave functions is dictated by the band

only ~ 0.25 eV higher[27] than the one in expanded GaP.) Thus, the lowest conduction wavefunction in a clustered $Ga_{0.5}In_{0.5}P$ alloy should segregate on the Ga-rich clusters as found in the calculation (Fig. 1). For electrons, the observed

ization, however, is less directly correlated with an atomic

in common-anion alloys can reduce the energy gap considerably with respect to the ideal random alloys. This is ac-

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shifts, which are 0.84, 0.61, and 0.77 eV, for $Al_{0.5}Ga_{0.5}As$, $Ga_{0.5}In_{0.5}P$, and $Al_{0.5}In_{0.5}As$, respectively. Note that energy *differences* such as optical bowing coefficients are not affected by this procedure.

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