Spatial Correlations in GaInAsN Alloys and their Effects on Band-Gap Enhancement and Electron Localization

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In contrast to pseudobinary alloys, the relative number of bonds in quaternary alloys cannot be determined uniquely from the composition. Indeed, we do not know if the Ga$_{0.}$ In$_{0.}$ As$_{0.}$ N$_{0.}$ alloy should be thought of as InAs + GaN or as InN + GaAs. We study the distribution of bonds using Monte Carlo simulation and find that the number of In-N and Ga-As bonds increases relative to random alloys. This quaternary-unique short range order affects the band structure: we calculate a blueshift of the band gap and predict the emergence of a broadband tail of localized states around the conduction band minimum.

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The need to simultaneously control both the band gap and the lattice constant of semiconductor alloys prompted interest in not only ternary (e.g., Ga$_{1-x}$In$_x$As) but also in quaternary (e.g., Ga$_{1-x}$In$_x$As$_{1-y}$P$_y$ [1], Ga$_{1-x}$In$_x$Asx

thought (e.g., Ref. [1]) that, in quaternary semiconductor alloys, one can simultaneously tune band gaps and the lattice constant by altering only the composition (x, y), we find that the ensuing band gap is, in fact, not unique and an additional thermodynamic variable ( ) controls it. (v) The level repulsion in the conduction band has an important consequence on localization: While the statistical distribution of As-centered As-$\mathrm{Ga}_m\mathrm{In}_{\,-m}$ tetrahedra in ternary InGaAs causes a small (1 meV) broadening of the conduction band minimum (CBM), the distribution of N-centered N-$\mathrm{Ga}_m\mathrm{In}_{\,-m}$ tetrahedra in GaInAsN leads to a far broader range (0 meV) of quasi-N-localized band tail states near the CBM. This wide range is due to the stronger perturbations by the higher energy cluster (L_{1c}-derived) levels in the nitride alloy. Such strong alloy band edge fluctuations can locally capture carriers, affecting carrier dynamics [6].

Our model energy functional depends both on site occupancy variables S_c, S_a and on atomic positions $\mathbf{R}_i$:

$$E((S_c\ S_a)\ (\mathbf{R}_i, i = 1, \ldots, M)) = E \qquad + E_{\ \mathrm{an}} . \tag{2}$$

Here $S_c = 1\ (-1)$ if Ga (In) is on cation site c, and $S_a = 1\ (-1)$ if As (N) is on the anion site a. Also, $(\mathbf{R}_i, i = 1, \ldots, M)$ are the atomic positions of all M atoms in the cell. Since we are not aiming at an accurate calculation of the absolute energy E but rather the atomic configuration $(S_c\ S_a)$ that has the best balance of strain vs bond energy, a simple energy functional is sufficient. We use

$$E \qquad = \frac{1}{2} \sum_i \sum_j^{nn} n_{i-j} e_{ij} \,, \tag{3}$$

where n_{i-j} is the number of bonds of type ij, and e_{ij} is the respective bond energy for which we use the experimental cohesive energy [5] of binary compound ij. For a ternary such as $\mathrm{Ga}_{1-x}\mathrm{In}_x\mathrm{As}$, the chemical energy E is a configuration independent constant $xE_{\ \mathrm{n}} \quad + (1 - x)E_{\ \mathrm{a}}$ and hence does not decide the thermodynamic energy balance. This is so because, in a ternary, any cation (Ga or In) atom is always bonded to As atoms, regardless of the configuration. For the strain energy we use the valence force field (VFF) model [7] and bond-stretching and bond-bending force constants of Refs. [8,9].

We start with the simplest case of $T = 0$. The energies of some limiting thermodynamic states, e.g., the

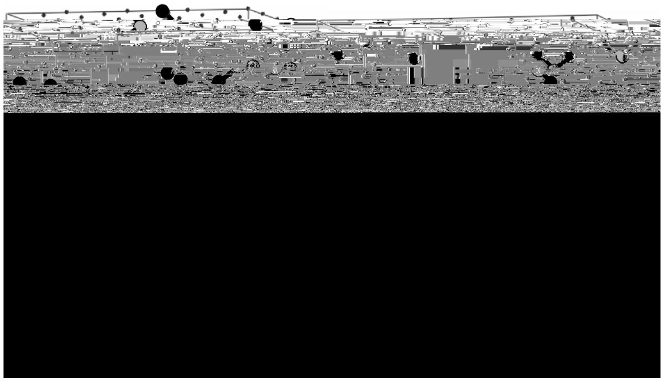

FIG. 2. A visualization of the real space supercell of the alloy Ga$_{0.}$ In$_{0.11}$As$_{0.}$ N$_{0.0}$ (a) for a random configuration and (b) with SRO determined by MC simulation at $T =$ 0 K. Note the preponderance of N-In Ga$_1$ and N-In clusters. Solid dots denote the positions of Ga and As atoms.

Figure 2 provides a visualization of the real space atomic positions in the supercell of Ga$_{0.}$ In$_{0.11}$As$_{0.}$ N$_{0.0}$ with SRO obtained with MC simulation at $T =$ 0 K. Taking statistics over many final configurations such as that shown in Fig. 2 reveals that *the main effect of SRO is that the concentration of the N-centered In Ga*$_1$ *clusters is statistically enhanced significantly (local In enrichment), whereas the In*

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