

Effects of atomic short-range order on the electronic and optical properties of GaAsN, GaInN, and GaInAs alloys

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Using large (~ 500 – 1000 atoms) pseudopotential supercell calculations, we have investigated the effects of atomic short-range order (SRO) on the electronic and optical properties of dilute and concentrated GaAsN, GaInN, and GaInAs alloys. We find that in concentrated alloys the clustering of like atoms in the first neighbor fcc shell (e.g., N-N in GaAsN alloys) leads to a large decrease of both the band-gap and the valence-to-conduction dipole transition-matrix element in GaAsN and in GaInN. On the other hand, the optical properties of GaInAs depend only weakly on the atomic SRO. The reason that the nitride alloys are affected strongly by SRO while GaInAs is affected to a much lesser extent is that in the former case there are band-edge wave-function localizations around specific atoms in the concentrated random alloys. The property for such localization is already evident at the dilute isolated impurity and impurity-pair limits.

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I. INTRODUCTION

GaN-based III-V semiconductors have recently attracted considerable attention due to their prospects in light-emitting device applications.^{1,2} Theoretical studies have addressed optical properties relevant to such technological applications, including alloy band-gap bowing (see Refs. 3–6 and references therein). However, these theoretical studies have assumed perfect random alloys, while clustering (the embryonic stage of phase separation) and fully developed phase separation have been observed experimentally in GaAsN (Ref. 7) and GaInN alloys,^{8–10} and are even thought to be responsible for the purple laser emission in GaInN.⁹ Clustering in nitride alloys is, in fact, expected since nitrogen in GaAs and indium in GaN have limited solid solubilities due to the significant strain energies resulting from the large size mismatch between the solute and solvent atoms.¹¹ Although the equilibrium *surface* solubility can be up to five orders of magnitude larger than in the bulk,¹² away from the surface, the stabilizing surface effect diminishes, and the homogeneous alloy is no longer stable, and could cluster or phase

Ga atoms at different positions in InN. We will explore the effects of such “elementary clusters” on the strain energy, localization, and band gap. We explore impurity pairs that are first, second, third, and fourth fcc neighbors. The physical properties of the impurity pairs are compared with those of the random case, as mimic by the average over *all* the possible configurations of the pairs. Such pair geometries were studied in the past in the context of nitrogen pair spectra in GaP ~Refs. 13–17! and in GaAs.¹⁸ The atomic relaxations and the strain energy are predicted by the valence force field ~VFF! approach^{19,20} using the parameters of Ref. 21. The electronic structure is calculated via an empirical pseudopotential method²² in a plane-wave basis. The

tution of a pair of impurities!, ~ii! bowing coefficients of the direct band gap, and ~iii! band-edge wave-function localization near the impurity atoms @f. Eq. ~4!#, for N-N pairs in GaAs and In-In pairs in GaN. We have placed the two impurity atoms in a 512-atom supercell in four configurations, namely, first, second, third, and fourth fcc neighbor positions ~denoted 1–4 in the figure!. Parts ~a! and ~d! of Fig. 2 show that N-N and In-In prefer the second neighbor positions ~largest lowering of strain energy!, while the first neighbor

We also find that the band-edge states and the band gap of Ga-Ga pairs in InN, Ga-Ga pairs in InAs, and In-In pairs in GaAs depend only very slightly on the geometries of the pairs. This is consistent with the fact that we find no localization of the band-edge states at the dilute impurity limits InN:Ga, InAs:Ga, and GaAs:In. For example, the first neighbor Ga-Ga pair in InN leads to a slight increase of the bowing coefficient by less than 0.2 eV -from 1.14 to 1.31 eV! with respect to the random case. On the other hand, the energy of the highest occupied level and the degree of localization for an As-As pair in GaN are found to depend

produces a decrease of the band gap of 122 meV (Fig. 4-a) corresponding to a variation of 12% with respect to the band gap of the random alloy and leading to a change in the bowing coefficient from 5.9 to 7.0 eV. The corresponding difference in band gap in $\text{Ga}_{0.875}\text{In}_{0.125}\text{N}$ alloys is 90 meV, corresponding to a variation of 3% with respect to the band gap of the random alloy and leading to a change in optical bowing coefficient from 2.4 to 3.2 eV. These bowing coefficients are larger than the previous theoretical result of 1 eV found for the random zinc-blende $\text{Ga}_{0.50}\text{In}_{0.50}\text{N}$ alloy.⁵ As a matter of fact, a bowing coefficient much larger than 1 eV has been indeed observed experimentally in $\text{Ga}_{1-2x}\text{In}_x\text{N}$ alloys, for indium compositions lower than 20%.³²⁻³⁴ The large sensitivity of nitride alloys to SRO suggests that experimental investigations of the generic effects of short-range order on material properties—which are very frequent in metallic alloys³⁵ but scant in semiconductor alloys; see recent review in Ref. 36! are best undertaken on nitride alloys. Indeed, this large sensitivity of the band gap to SRO has been observed experimentally in GaInN alloys: the formation of indium-rich clusters in $\text{Ga}_{1-2x}\text{In}_x\text{N}$ alloys with x [10–20% leads to a decrease of the band gap by 170–250 meV with respect to the band gap of the random alloy.⁹ The existence of SRO may also explain the different values found experimentally for the band gap of $\text{GaAs}_{1-2x}\text{N}_x$ alloys having the same nominal nitrogen composition but grown under different conditions.^{37,38}

C. The band-edge wave-function localizations

Mader and Zunger³¹ showed that large clustering in GaAlAs and GaInP alloys leads to a decrease of the direct band gap accompanied by an enhancement of band-edge wave-function localizations. In line with that, we analyze the trends of the optical properties with SRO in terms of wave-function localization: Fig. 5 shows $P_{\text{VBM}}(\mathbf{G})$ and $P_{\text{CBM}}(\mathbf{G})$

(Eq. 3) in the three alloys studied here. It demonstrates that indeed the behavior of the band-gap and the momentum matrix element are correlated with band-edge wave-function localizations: As a_1 increases, the VBM and CBM wave functions of $\text{GaAs}_{0.875}\text{N}_{0.125}$ alloys localize more (e.g., $P_{\text{VBM}}(\mathbf{G})$ and $P_{\text{CBM}}(\mathbf{G})$ decrease), while, at the same time, the band gap and the momentum matrix element both decrease (Figs. 4-a) and 4-b). By calculating the atom-resolved localization parameter $Q_{b,i}$ (Eq. 4), we can find where the localization occurs. Figure 6-a) shows that the localization of the CBM is strongest around the nitrogen atoms. Similarly, we found that the localization of the VBM is strongest around the arsenic atoms.³

In contrast to the case of $\text{GaAs}_{0.875}\text{N}_{0.125}$, Figs. 5-e) and 5-f) indicate that the band-edge states of $\text{Ga}_{0.875}\text{In}_{0.125}\text{As}$ alloys are extended and so do not depend on the SRO a_1 parameter. This is evident by the fact that $P_{\text{VBM}}(\mathbf{G})$ and $P_{\text{CBM}}(\mathbf{G})$ are large (around 99%) and independent of a_1 , and by the fact that the real-space localization parameters for the CBM of $\text{Ga}_{0.875}\text{In}_{0.125}\text{As}$ are only weakly dependent on the SRO (cf. Fig. 6-a). This extended nature of the GaInAs band-edge states thus implies the insensitivity of both the band gap and the momentum matrix element with SRO (Figs. 4-e) and 4-f).

The situation of $\text{Ga}_{0.875}\text{In}_{0.125}\text{N}$ is intermediate between that of $\text{GaAs}_{0.875}\text{N}_{0.125}$ and $\text{Ga}_{0.875}\text{In}_{0.125}\text{As}$, in the sense that only one band-edge state depends on the SRO: clustering in $\text{Ga}_{0.875}\text{In}_{0.125}\text{N}$ leads to a larger localization of the VBM (p

tion is consistent with the decrease of the band gap and the decrease of the momentum matrix element as a_1 increases (Figs. 4-c! and 4-d

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