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 method[22] 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 @cf. 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

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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