Giant and Composition-Dependent Optical Bowing Coefficient in GaAsN Alloys

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Using first-principles supercell calculations we find a giant (7–16 eV) and composition-dependent optical bowing coefficient in $GaAs_{1-x}N_x$ alloys. We show that both effects are due to the formation

The electronic structures of the alloys are calculated by the LDA as implemented by the relativistic linearized augmented plane wave method [13]. The Ga $3d$ states are treated as valence bands. The calculated lattice constants of the end-point compounds a_{GaAs} - $\mathbf{5.64}$ Å and a_{GaN} - $\mathbf{4.51}$ Å are close to the experimental values [1]. For the relaxed alloys, we find that lattice constants vary linearly as function of composition x. The equilibrium bond lengths $R_{\mathrm{Ga\text{-}As}}$ and $R_{\mathrm{Ga\text{-}N}}$ show the typical bimodal distribution. The average bond length relaxation parameter [14] e - $[R_{\mathrm{Ga\text{-}As}}(x)$ 2 $R_{\mathrm{Ga\text{-}N}}(x)]/[R^0_{\mathrm{Ga\text{-}As}}$ 2 $R^0_{\mathrm{Ga\text{-}N}}]$ is close to 0.67 (e - $\mathbf{0}$ indicates no relaxation, while e - $\mathbf{1}$ indicates full relaxation).

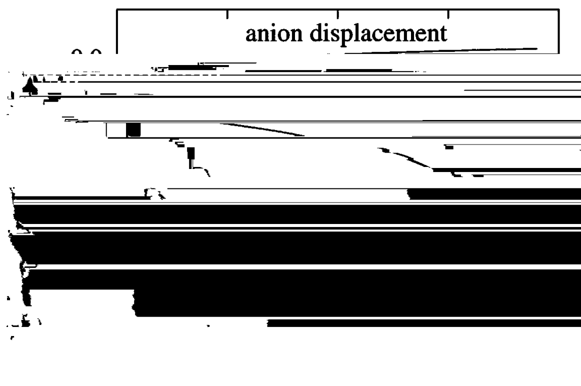

FIG. 1. Calculated band gap change DE_g as function of atomic displacement d for GaAs. The results are calculated using a CuAu-like Ga_2As_2 structure, in which the two Ga-As bond lengths are given by $R_{\text{Ga-As}}$ - [0.125 1 (0.25 6 d)^2]$^{1/2}a$, where a is the lattice constant. The crystal field averaged band gap increases when the anion is displaced, but decreases significantly when cation is displaced.

(ii) GaAs and GaN volume deformed to the value for the alloy, (iii) unrelaxed GaAsN, and (iv) relaxed GaAsN. We observe that (a) the VBM wave function becomes localized on As as we combine GaAs with GaN in the CE step, and that significant further localization on As takes place in the SR step. At the same time, the VBM wave-function amplitude on N is severely reduced at the SR step. (b) The CBM wave function becomes strongly localized on N upon forming the alloy in the CE and SR steps. Thus the formation of GaAsN from GaAs 1 GaN shifts valence charge from N to As, while the conduction charge shifts in the opposite direction from As to N. This creates large b_{CE} and b_{SR}.

To understand further the large SR term, we recall that [17] the principle static atomic displacement pattern in mixed-cation alloys (e.g., GaInP) is due to anion motion, while in mixed-anion alloys (e.g., GaAsN) the principal motion is due to the cation. We can separate the CE contribution from SR contribution by considering the changes in the band gap of *pure* GaAs (where $b_{\text{CE}} \equiv 0$) in response to displacing anions and separately cations (Fig. 1). We find that cation displacements lower the band gap considerably more than anion displacements, in accord with the trend in b_{SR} seen in Table I. This reflects the fact that cation displacements lead to strong intraband coupling

suggest that in semiconductor alloys the band gap variation as function of x can be divided into two regions: (i) a bandlike region where the bowing coefficient is relatively small and $\Delta E_g(x)$ can be described by Eq. (1) with nearly constant b, and (ii) an impuritylike region where the bowing coefficient is relatively larger and composition dependent. We conjecture that the existence of localized band edge wave functions is unique to alloy systems exhibiting in the dilute limit a "deep" impurity state. As is well known [18], isovalent impurities such as $\underline{\mathrm{Ga}}$As:Al, Ga$\underline{\mathrm{As}}$:P, Si:Ge, or Zn$\underline{\mathrm{Se}}$:S usually have a weak central-cell potential $\Delta V \equiv V_{\mathrm{host}} - V_{\mathrm{impurity}}$ and produce energetically shallow and spatially extended states. In this case of weak ΔV, as the impurity concentration increases, the impurity wave functions start to overlap and the impurity energy level merges almost immediately with the band edges and both move rigidly and continuously with x, producing "optical bowing" of the type described by Eq. (1).