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Band gaps of GaPN and GaAsN alloys

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The importance of atomic relaxations, chemical disorder, and epitaxial constraints on the band gap of random, anion-mixed nitride alloys GaPN and GaAsN have been investigated, via pseudopotentials calculation. It has been demonstrated that simple approximations such as the virtual crystal approximation, or the use of high-symmetry ordered structure to mimic a random alloy, or the neglect of atomic displacements, are inadequate. It is found that a fully relaxed, large supercell calculation reproduces well the experimental band gaps of GaPN and GaAsN films.
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Alloys of mixed-anion nitrides GaP–GaN and GaAs–GaN are different from most isovalent alloys, such as GaP–InP, GaAs–GaSb and GaAs–AlAs, in that the former systems exhibit in the dilute limit *deep band gap impurity levels*. Figure 1 shows the pseudopotential calculated,[1,2] energy levels of relaxed isolated substitutional anion impurities in GaN, GaP and GaAs. We see that when the atoms surrounding the impurity are allowed to relax, the P and As

The whole calculation is then repeated for different alloy compositions. This gives us the band gap versus composition curves shown as solid lines connecting solid dots in Fig. 2. This type of calculation allows for the following physical effects: (1) wave function localization,[1,2] (2) atomic relaxation, (3) multiband coupling, and (4) the existence of a distribution of many local chemical environments (e.g., Ga coordinated by N_4, N_3P, N_2P_2, NP_3 and P_4) found previously to be crucial[11] for a correct description of the random alloys. This calculation neglects, however, short-range order in the form of atomic clustering. This effect will be discussed in a separate publication.[12]

To shed some light on the relative importance of physical factors affecting the composition dependence of the band gap, we now take a few steps backwards, and resolve our ‘‘bottom line result’’ into its simpler ingredients.

First, we imagine a crude model of the alloy in which only hydrostatic effects are taken into account: We model the ‘‘volume-deformated’’ (VD) band gap (of $\mathrm{GaP}_{1\,2\,x}\mathrm{N}_x$, for example) as

$$E_g^{\mathrm{VD}}(x)\ 5\ (1\ 2\ x$$

and the unrelaxed supercell calculations[8,9] are inappropriate for GaPN and GaAsN.

(iii) We next tested the ‘‘special quasirandom structures’’ (SQS) idea.[14] In this approach a small supercell with low site symmetry is designed to statistically mimic the atomic correlations in far larger *random* structures. Using the SQS-8 (SQS-16) structure (Ref. 11) we find band gaps of 1.23 (1.09) eV in $GaP_{0.5}N_{0.5}$ and of 0.44 (0.37) eV in $GaAs_{0.5}N_{0.5}$, which compared favorably with the 512 atom supercells calculation of 1.14 ± 0.07 eV and 0.39 ± 0.08 eV. Thus, the SQS construct is highly effective in that small, but specially selected unit cells reproduce remarkably well large unit cells.

Having understood the importance of relaxation, chemical effects and disorder on the band gap, we next compare our results with experiment. Since current experiments[16–20] are done on epitaxial films rather than on bulk alloys, we repeat our bulk calculation (Fig. 2) for epitaxial geometry. This is done by restricting the in-plane lattice constant to match that of the prescribed substrate (GaP for GaPN alloys, and both GaAs and GaP substrates for GaAsN alloys), and relaxing the supercell lattice constant in the tetragonal direction so as to minimize the energy. We thus assume *coherent* films, while in reality some of the coherence could be lost, depending on the thickness and on the composition of the films. We further correct our calculated $T = 0$ K alloy results of Fig. 2 to room temperature used in Refs. 15 and 17. We do so by using a composition-weighted band gap temperature shift of the constituents: 0.10 eV for GaP and GaAs, and 0.18 eV for GaN (measured[20,21] from low temperature to 300 K). We have also shifted the experimental results of Refs. 16, 18, and 19 to correct for the temperature dependence of the band gap from 5 K[16] or 77 K[18,19] to room temperature. Figure 3 shows our calculated, fully relaxed and temperature-corrected band gaps of $GaP_{1-x}N_x$ and $GaAs_{1-x}N_x$ in both epitaxial and in bulk geometries, compared with the measured results.[15–19] We see that the epitaxial conditions can change considerably the band gap of these alloys with respect to the bulk conditions. We also notice quite good agreement between our epitaxial calculations and experimental results, especially for larger N compositions.

In summary, we have pointed out that simple approximations such as the VCA, the use of high-symmetry small ordered structures to mimic random alloys, or the neglect of relaxation are inappropriate for describing the band gaps versus composition dependence in GaPN and GaAsN random alloys. This is due to the fact that these kinds of calculations misrepresent the band-edge wave function localization occurring in these alloys.[1–3] In addition, we found that our fully relaxed, large supercell calculations of epitaxial GaPN and GaAsN alloys differ considerably from the corresponding bulk results, and reproduce quite well the measured band gaps.

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