Deep nitrogen-induced valence- and conduction-band states in GaAs$_{1-x}$N$_x$

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louin zone treating the Ga d electrons as valence states, using the Perdew–Zunger[9] local density approximation (LDA) exchange-correlation potential, and a kinetic energy cutoff of 400 eV which implies more than 25,000 plane waves per **k** point. The crystal volume was optimized with respect to total energy, and the internal atom positions were relaxed jwith both the conjugate-gradient

sion spectra from N $1s$ for GaN and GaAsN. The matrix elements were included. We see similar features as in Figs. 1(c) and 1(d) where no matrix elements were included. Specifically, the two valence-band peaks at $E_v(\mathrm{GaAsN}) - (2.5–5.0)$ eV in GaAsN match the peaks in GaN at $E_v(\mathrm{GaAsN}) - (2.5–5.0)$ eV. These calculated peaks also

GaN (Fig. 2) at $E_v(\text{GaAsN}) - 399$ eV. Thus, the core-hole energies in GaAsN and GaN align approximately both at the N $1s^2$ LDA level and at the broken symmetry level. This is illustrated in Fig. 2.

Figure 4 shows the calculated wave function squared of GaAs$_{0.97}$N$_{0.03}$ near the VBM and near the CBM. We see that there is significant N and As character in both band edges contrary to the suggestion of of Ref. 3. Thus, interband transitions need not be weak. To examine this point we have calculated the valence-band→conduction-band absorption spectrum (Fig. 5) of GaAsN and GaAs. Indeed, no significant weakening of the threshold absorption is noted upon adding N to GaAs.

The origin to the deeper N p valence-band states in GaAsN compared to corresponding As p states [Fig. 1(b)] is the short N–Ga bond length. We show this by starting from the unrelaxed bond geometry (N replacing As and all bonds kept at the Ga–As bond length of 2.428 Å) and then gradually allowing the Ga atoms next to N to relax inwards, form-

at $E_v(\text{GaAsN}) - 6.9$ eV. As a consequence of the deeper N p valence-band states in GaAsN, also the N p conduction-band states are lowered [Fig. 6(a)] as the N–Ga bond length is reduced. Thus, we expect to find N p closer to the CBM than for the corresponding As p states. The VBM level is almost unaffected by variations of the N–Ga bond length since the VBM is As p like.

We conclude that N substitution in GaAs introduces bonding valence states around $E_v(\text{GaAsN}) - 2.5$ to $E_v(\text{GaAsN}) - 5.0$ eV, at approximately the same location as the bonding N states in pure GaN, when the GaN/GaAs valence-band alignment is taken into consideration. In addition, N induces antibonding states inside the conduction band at energies above $E_v(\text{GaAsN}) + 1.5$ eV. The effects of these states on the valence-band→conduction-band absorption spectra are negligible.

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