

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

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Most studies of the anomalous electronic properties of the $\text{GaAs}_{1-x}\text{N}_x$ alloy have focused on *near-edge* states, but x-ray spectroscopic experiments [V. N. Strocov *et al.*, Phys. Status Solidi B **233**, R1 (2002)] have now revealed anomalous properties deep inside the valence and conduction bands. Indeed, whereas N *p* character is found in GaN in the energy region near the valence-band maximum (VBM), when $\sim 3\%$ N is introduced into GaAs one finds that N *p* character exists about 2–3 eV *below* the VBM and as two narrow peaks just above the conduction-band minimum. First-principles calculations of the N *p* character in $\text{Ga}_{32}\text{As}_{31}\text{N}$ and GaN show that the valence resonances are due the fact that the VBM of $\text{GaAs}_{0.97}\text{N}_{0.03}$ itself lies > 2 eV above that of GaN. Thus, there is no need to involve an N \rightarrow As charge transfer to explain the data. This conclusion is further confirmed by our calculated valence \rightarrow conduction-band absorption spectra. We also show that the broken-symmetry core-hole calculations are necessary to explain, within the local density approximation (LDA), the energy of the N $1s\leftarrow$ valence-band transitions. As to the conduction-band peaks observed experimentally in the x-ray absorption, our LDA calculations do not reveal the sharp peaks seen in the measured spectra, leading to the possibility that the latter may not be related to substitutional N.

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The electron structure of $\text{GaAs}_{1-x}\text{N}_x$ has attached considerable attention¹ because of its potentially useful anomalies relative to conventional isovalent III-V alloys such as $\text{GaAs}_{1-x}\text{N}_x$ and $\text{Ga}_{1-x}\text{In}_x\text{As}$. These anomalies include giant band-gap bowing, as well as wave-function localization.² Since the favored experimental probe used most often was near-edge emission [photo luminescence (PL)], the anomalies detected and the calculations performed² were restricted to states near the valence-band maximum (VBM) E_v and conduction-band minimum (CBM) E_c . Both experiment¹ and theory² showed that localization occurred primarily near the CBM. One wonders, however, whether one might find the fingerprints of nitrogen substitution deep inside the valence or conduction bands. Until recently, this spectral range, which is not accessible by PL, was unexplored. Recently, soft x-ray (~ 400 eV) absorption and emission experiments between the N $1s$ core and the N final *p* state deep in the valence and conduction bands were conducted by Strocov *et al.*³ They find that (i) whereas in pure GaN the N $1s\leftarrow$ valence-band emission transitions have a strong peak near the VBM, in $\text{GaAs}_{0.97}\text{N}_{0.03}$ this peak is shifted to $\sim 2\text{--}3$ eV below the VBM. The authors interpreted this shift as reflecting a displacement of VBM charge from the nitrogen atom (in GaN) to the As atom (in $\text{GaAs}_{0.97}\text{N}_{0.03}$). Furthermore, they observe that (ii) the N $1s\rightarrow$ conduction-band absorption transitions in GaAsN occur at 1–2 eV below the corresponding transitions in pure GaN which is at $\geq E_c(\text{GaAsN}) + 3$ eV. They interpret these states as being N localized. Because effect (i) suggested to the authors As-localized VBM, whereas effect (ii) suggested N-localized CBM, they³ proposed that the VBM \leftrightarrow CBM transitions in GaAsN are particularly weak due to the fact that carriers are localized on different anion sublattices.

In this work we explore theoretically the N-induced electronic structure deep inside the GaAsN valence band and find, in agreement with experiments, nitrogen states at and below $\sim E_v(\text{GaAsN}) - 2$ eV whereas the N-induced charges

at the VBM itself are small as previously noted.² However, these states do not reflect any inter sublattice (N \rightarrow As) charge transfer,³ but mirror instead the fact that the GaN VBM lies itself about 2 eV below the GaAs VBM [i.e., the GaAs/GaN valence-band offset is ~ 2 eV (Ref. 4)]. These nitrogen-localized valence states constitute the bonding counterpart to the conduction-band localized antibonding states. Indeed we find N *p* states to be inside the conduction band of GaAsN, analogous to the $t_2(L_{1c})$ state noted by Mattila *et al.*⁵ Our calculated soft x-ray absorption and emission spectra compares well with experiments. Our calculated valence-band \leftrightarrow conduction-band optical absorption also shows that the transitions are not particularly weak, consistent with the fact that both VBM and CBM have charge densities on N and As sites. We do not agree with the experiment on the two *sharp* and narrow peaks seen near the CBM or within the band gap.

We first calculate the N $1s\leftrightarrow$ valence-band and N $1s\leftrightarrow$ conduction-band spectra without creating a N $1s$ hole, i.e., by computing dipole-matrix elements weighted by joint densities of states (DOS). This is justified in this case by the absence³ of core-hole effects in the measured spectra. Our calculations are represented by a 64-atom supercell with one N replacing an As atom (i.e., $x \approx 3\%$). The optical properties in terms of the *l*-decomposed DOS and x-ray absorption and emission as well as the valence- to conduction-band absorption were obtained from a full-potential linearized-augmented-plane-wave (LAPW) method⁶ adopting a scalar-relativistic Hamiltonian. We chose a plane-wave cutoff determined by $R_{mt}K_{max} = 7.8$, where $R_{mt} = 1 \text{ \AA}$ is the nitrogen muffin-tin sphere radius. The DOS, x-ray spectra,⁷ and absorption coefficient were calculated, using the tetrahedron integration method with 56 **k** points (and including inversion symmetry) in the irreducible Brillouin zone and applying a Gaussian broadening of 25 meV. The relaxed atomic positions for LAPW were computed using ultrasoft pseudopotentials⁸ with ten **k** points in the irreducible Brillouin zone.

lounin zone treating the Ga *d* electrons as valence states, using the Perdew–Zunger⁹ 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-gradient¹⁰ and quasi-Newton¹¹ algorithms.

In addition to the no-core-hole calculations we have also performed supercell calculations with one out of a few nitrogen atoms excited to the Slater transition-state configuration $1s^{1.5}$. The 0.5 electron is placed in a background of uniform jellium (divided into 1/4 spin up and 1/4 spin down); the remaining 1.5 electron is divided into 3/4 spin up and 3/4 spin down. The calculation is iterated to self-consistency. This “symmetry-broken” approach^{12,13} provides realistic excitation energies and includes core-hole electron effects.

Figure 1(a) shows the total DOS of pure GaAs, showing, in order of decreasing binding energies, the Ga 3*d* band at $E_v(\text{GaAsN}) - 15$ eV, the As *s* band at $E_v(\text{GaAsN}) - 12$ eV, the main valence band consisting of a lower $E_v(\text{GaAsN}) - 6$ eV branch of Ga *s* and an upper Ga and As *p* branch between $E_v(\text{GaAsN}) - 4$ eV and $E_v(\text{GaAsN})$. The conduction band consists of the Ga *s* peak at $E_v(\text{GaAsN}) + 2$ eV and three Ga, As *p* peaks at higher energies. Substitution of one As in $\text{Ga}_{32}\text{As}_{31}\text{N}$ by N reduces the cation-anion bond length from 2.428 Å (Ga–As) to 2.038 Å (Ga–N), closer to the natural Ga–N bond (1.94–1.97 Å) in pure GaN. Figures 1(b) and 1(c) show the N *p* density of states enclosed within the N muffin-tin region. This figure indicates that this substitution leads to two N-induced *p*-like valence states in the region between $E_v(\text{GaAsN}) - 2.5$ eV and $E_v(\text{GaAsN}) - 5.0$ eV. Comparison of the N-induced *p*-like peaks in $\text{GaAs}_{0.97}\text{N}_{0.03}$ [Fig. 1(c)] with the corresponding N *p*-like peaks in pure GaN [Fig. 1(d)] shows similarity. We have aligned the VBM’s in Fig. 1 according to the LDA-calculated unstrained valence-band offsets $\Delta E_v(\text{GaAs}/\text{GaN}) = 2.2$ eV and a type I $\Delta E_v(\text{GaAs}/\text{GaAs}_{0.97}\text{N}_{0.03}) \approx 0.05$ eV². We see that the *p*-like N-induced valence band in GaAsN at $E_v(\text{GaAsN}) - (2.5-5.0)$ eV is approximately aligned with the *p*-like N band in GaN at $E_v(\text{GaAsN}) - (2.5-5.0)$ eV = $E_v(\text{GaN}) - (0.3-2.8)$ eV. Hence, the ~2 eV shift noted by Strocov *et al.*³ is a natural consequence of the relative band alignment, shown schematically in Fig. 2 using the measured values of the band gaps.^{14,15} Note that once the VBM’s of different host materials are aligned (Fig. 2), the two N 2*s* and Ga 3*d* transitions in GaAsN, and GaN align approximately as well.¹⁶ As noted in Ref. 16, only localized states follow the alignment rule.

Regarding the nitrogen-induced *p* states inside the GaAsN conduction band [Fig. 1(c)], we observe a rather constant distribution in energy of these states with peaks at $E_c(\text{GaAsN}) + 1.5, +2.0, +4.9,$ and $+6.8$ eV. Those states are due to GaAs L_{1c} and X_{1c} states with *p* character, perturbed and split due to nitrogen substitution.² Our calculation shows indeed that *p* character in the conduction band comes from the **k** point away from the Γ , as the nitrogen states at the Γ point is *s* like in the conduction band.

Figure 3 shows the calculated x-ray absorption and emis-

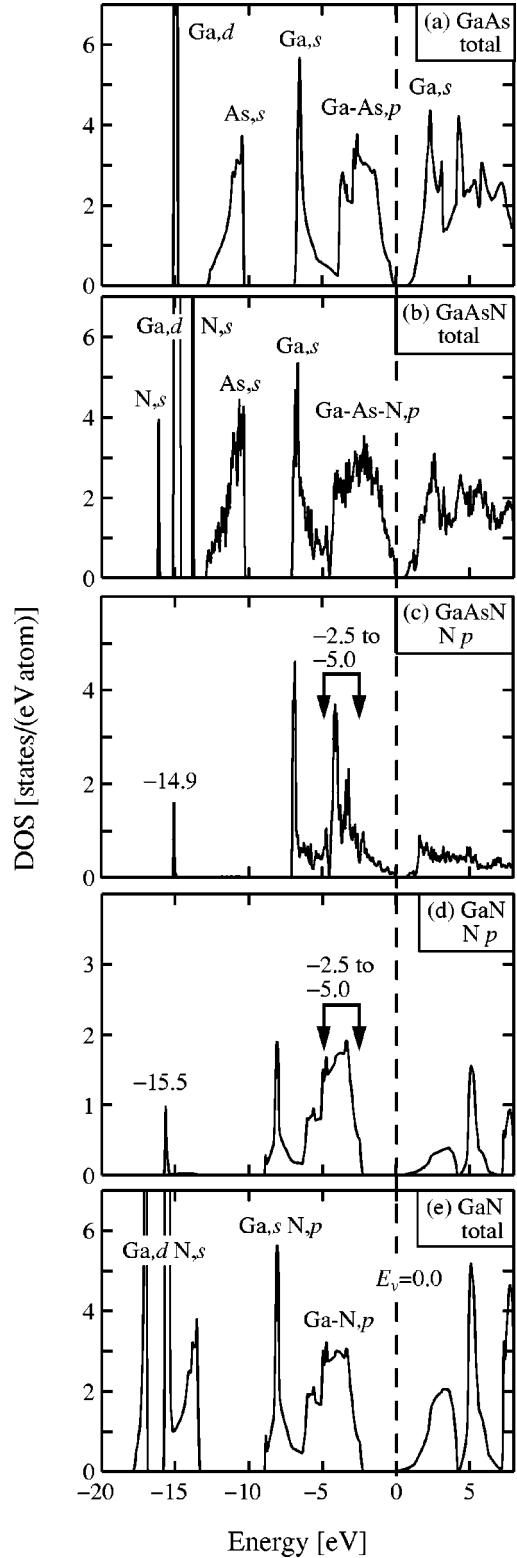


FIG. 1. Total and local DOS of GaAs, $\text{Ga}_{32}\text{As}_{31}\text{N}$, and GaN. The energy zero is the VBM of GaAsN whereas the VBM of the other materials is shifted by the corresponding unstrained band offsets. (a), (b), and (c) show total DOS per atom, whereas (c) and (d) show the *p*-like DOS of the nitrogen atom. The atomic sphere radii used for defining local DOS were $R_{mt}(\text{N}) = 0.93$ and 0.99 Å in GaN and GaAsN, respectively. The arrows in part (c) and (d) denote the N *p* states in the valence bands of GaAsN and GaN.

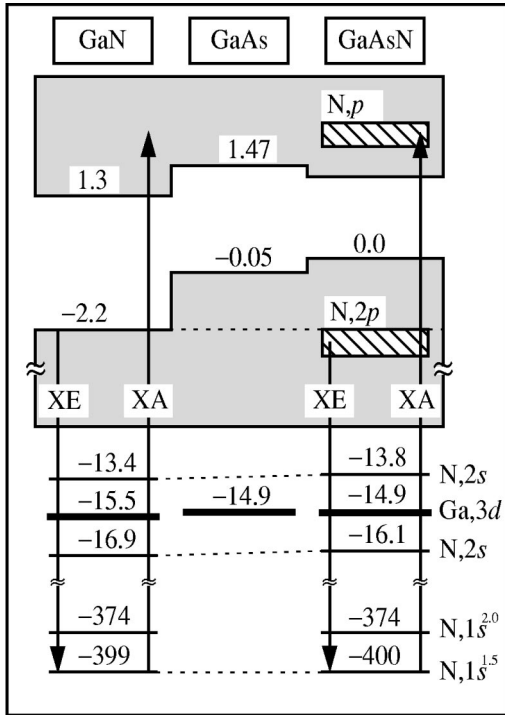


FIG. 2. Schematic figure of the x-ray emission (XE) and absorption (XA) in GaN, GaAs, and $\text{Ga}_{32}\text{As}_{31}\text{N}$, on an absolute energy scale with $E_v(\text{Ga}_{32}\text{As}_{31}\text{N}) = 0$ eV. The core-state energies are LDA results, the calculated valence-band offsets are from Ref. 4, and the band-gap energies are experimental data (Refs. 14 and 15).

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 $E_v(\text{GaAsN}) - (2.5-5.0)$ eV in GaAsN match the peaks in GaN at $E_v(\text{GaAsN}) - (2.5-5.0)$ eV. These calculated peaks also match with the experimental^{3,17} broad absorption peak of both GaAsN and GaN when VBM alignment is taken into account. The small N p contribution to the emission near the VBM in GaAsN is due to hybridization with As p. Also the calculated peak at $E_v(\text{GaAsN}) - 6.9$ eV in GaAsN and $E_v(\text{GaAsN}) - 8.0$ eV in GaN agrees well with the measured³ absorption peak at about $E_v(\text{GaAsN}) - 7.4$ eV. This peak arises from N p hybridizing with Ga s. From the calculated x-ray absorption spectra of the conduction band, we see a more abrupt onset to absorption in GaAsN than in GaN. Thus, the N p states are localized more closer to the CBM in GaAsN. We cannot identify the two sharp measured³ conduction-band peaks in GaAsN however, the calculated conduction-band N p peaks in GaN are consistent with measured absorption spectra.^{3,17}

In order to check if the existence of a core hole (neglecting in the previous calculations leading to Figs. 1–3) can significantly distort our results, we have performed a broken-symmetry calculation^{12,13} for pure GaN. To mimic the formation of a N 1s core hole we consider a Ga_4N_4 supercell where one nitrogen atom contains a 1s core hole, whereas the other three nitrogen 1s levels are fully occupied $1s^2$. We iterate this solution to self-consistency, insisting on a total of

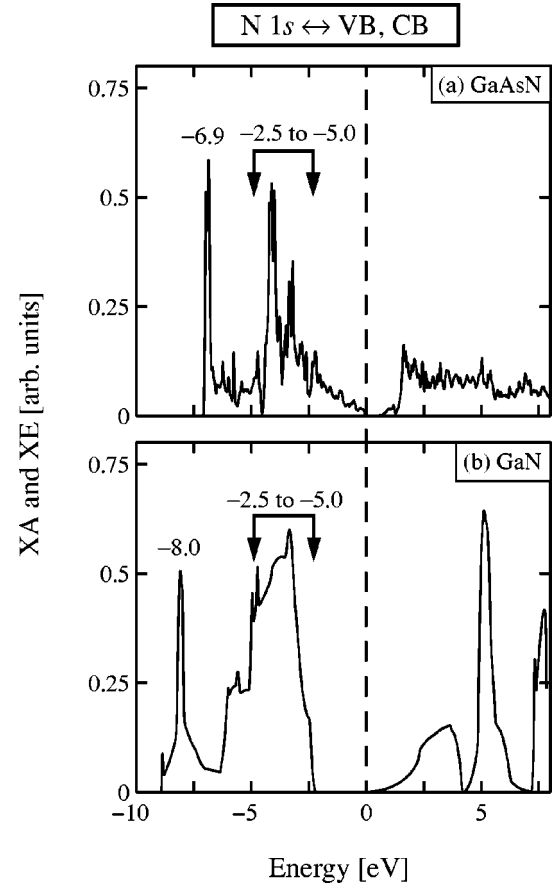


FIG. 3. Calculated LDA x-ray emission (XE) and absorption (XA) spectra of N 1s K line in $\text{Ga}_{32}\text{As}_{31}\text{N}$ and GaN, on an absolute energy scale with $E_v(\text{Ga}_{32}\text{As}_{31}\text{N}) = 0$ eV.

one hole in the supercell 1s state. We find that when a core hole is absent in the broken-symmetry calculation, the N 1s band consists of fourfold-degenerate narrow state at $E_v(\text{GaN}) - 372$ eV = $E_v(\text{GaAsN}) - 374$ eV (Fig. 2). When a core hole is present on a single nitrogen atom and self-consistent spin-restricted calculations are converged with this configuration, we find a threefold degenerate N $1s^2$ band at $E_v(\text{GaN}) - 372$ eV (close to the $1s^2$ LDA result of GaAsN) plus a split-off N $1s^{1,5}$ band at $E_v(\text{GaN}) - 397$ eV = $E_v(\text{GaAsN}) - 399$ eV which contains the hole. This approximately self-interaction corrected energy is close to the measured¹⁷ value $\sim E_v(\text{GaN}) - 400$ eV, but is very different from $E_v(\text{GaN}) - 372$ eV obtained by the ground state $1s^2$ LDA calculations. We examined the affects of the core hole on the conduction-band energies. We find that the core hole lowers the CBM by ~ 0.4 eV (a core hole-conduction electron excitonic binding), suggesting rather weak core-hole perturbation on the conduction band. This shows that whereas a core-hole affects considerably the core energy level [$E_v(\text{GaN}) - 397$ eV instead of $E_v(\text{GaN}) - 372$ eV in LDA], it does not change much the valence or conduction states.

We have also performed core-hole calculations for GaAsN. We find that the split-off N 1s level containing the hole is at $E_v(\text{GaAsN}) - 400$ eV, close to the value in pure

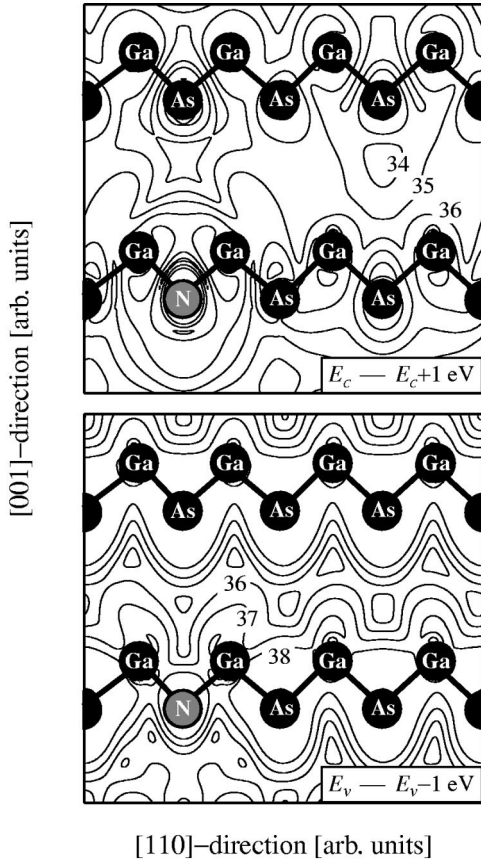


FIG. 4. Contour plot of the wave function squared near the VBM and near the CBM. Logarithm values in \AA^{-3} are given.

GaN (Fig. 2) at $E_v(\text{GaAsN}) - 399 \text{ eV}$. 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 $\text{GaAs}_{0.97}\text{N}_{0.03}$ 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 Ref. 3. Thus, interband transitions need not be weak. To examine this point we have calculated the valence-band \rightarrow 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 \AA) and then gradually allowing the Ga atoms next to N to relax inwards, forming finally the equilibrium N-Ga bond length of 2.038 \AA . The change in eigenvalues and DOS are shown in Fig. 6 with respect to the VBM of the relaxed GaAsN. We see that before inward relaxation of the Ga, the N p states in GaAsN are near the VBM with energy peak at $E_v(\text{GaAsN}) - 0.9 \text{ eV}$, just as the As p states are in GaAs. As the Ga atoms relax towards the nitrogen impurity, the deep Ga $3d$ at $E_v(\text{GaAsN}) - 15 \text{ eV}$ stays fixed, but the N p valence-band

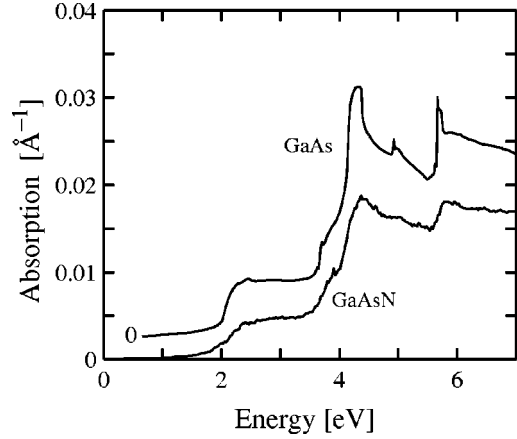


FIG. 5. Calculated LDA absorption coefficient of $\text{Ga}_{32}\text{As}_{31}\text{N}$ and GaAs, normalized to the GaAsN unit-cell volume.

states move to deeper energies, forming finally two N p peaks at $E_v(\text{GaAsN}) - 3.0 \text{ eV}$ and $E_v(\text{GaAsN}) - 4.1 \text{ eV}$. At the same time, a new Ga s -N p peak starts to gain intensity as the N-Ga bond length is reduced, finally forming a state

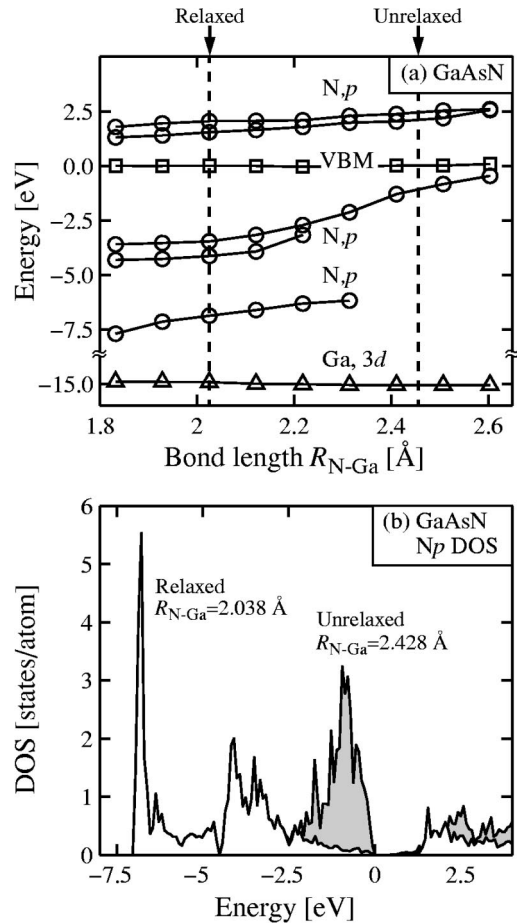


FIG. 6. (a) Ga $3d$ energy level (triangles), N p -like DOS energy peaks (circles), and VBM energy (squares) vs N-Ga bond length in GaAsN. Dashed lines indicate the N-Ga bond lengths 2.038 \AA and 2.428 \AA . All energies are referred to the VBM of relaxed GaAsN. (b) N p -like DOS of GaAsN for N-Ga bond lengths 2.038 \AA and 2.428 \AA (shaded).

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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