Ab initio study of substitutional nitrogen in GaAs

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(Received 12 October 2000; accepted for publication 30 December 2000)

We investigate the atomic geometry, formation energies, and electronic structure of nitrogen occupying both arsenic and gallium sites in GaAs (N_{As} and N_{Ga}) using first-principles total-energy calculations. We find that both neutral defects induce impurity-like empty levels in the band gap acting as acceptors. While N_{As} shows a *s*-like a_1 level in the middle of the band gap, N_{Ga} shows a *p*-like t_2 level close to the bottom of the conduction band. The gap level of N_{As} gives theoretical support for the experimentally observed band-edge redshift on the GaAsN alloy for a N concentration ~3%. Strong inward relaxations preserving the T_d symmetry characterize the N_{As} equilibrium geometry in all the charge states investigated. In contrast, N_{Ga} exhibits a structural metastability in neutral charge state and Jahn–Teller off-center distortions in negative charge states forming a negative-*U* center. Formation energies of competing N_{As} and N_{Ga} defects are also discussed. © *2001 American Institute of Physics.* [DOI: 10.1063/1.1351524]

Recently, the mixed group V alloy GaAsN has attracted great attention because its composition-dependent physical properties. The narrowing of the band gap with the increase of the nitrogen concentration in this alloy has been measured and calculated.[1,2] This property may allow the fabrication of optical devices covering the entire range of the visible spectrum. However, the electronic and structural properties of the isolated N impurity in GaAs which corresponds to the dilute limit of GaAsN are poorly understood.

Early photoluminescence (PL) studies on N-doped GaAs under hydrostatic pressure[3,4] have identified an excitonic recombination associated to N as an isoelectronic impurity in GaAs. Moreover, theoretical studies on $GaAs_{1-x}N_x$ ($x \sim 0.4\%$) by Bellaiche *et al.*[5] have suggested that N occupying an As site induces a resonant impurity level in the bottom of the conduction band. They also suggest that the observed PL emissions are due to this resonant impurity level which enters into the fundamental gap when pressure is applied. However, more recent PL studies[6,7] on $GaAs_{1-x}N_x$ at low concentrations ($x<0.01\%$) have reported sharp PL emissions showing that nitrogen would induce levels inside the band gap independent if pressure is applied. However, the N concentration close to the dilute limit appears to be a crucial parameter in the GaAsN alloy.

In this work we study the isolated N impurity at both anion and cation sites in GaAs (N_{As}, N_{Ga}) from first-principles total-energy calculations. Our theoretical approach is based on the density-functional theory[8] within the local-density approximation (LDA).[9] Ga, As, and N atoms are described by norm-conserving soft pseudopotentials[10] considering the *p* orbital as the local component and a plane-wave energy cutoff of 45 Ry. In order to ensure a good description for GaAs and GaAs:N, effects due to the Ga $3d$ electrons were included using the nonlinear core correction.[11] We use a fully relaxed 32-atom supercell without any symmetry constrains. The forces at the ions are considered converged for values at any force coordinate less than 0.05 eV/Å. For the Brillouin zone sampling we use a $2\times2\times2$ Monkhorst–Pack mesh[12] corresponding to four **k** point. We also performed calculations for neutral N_{As} and N_{Ga} with a larger 64-atom supercell including two points for the Brillouin zone sampling [Γ and $(\frac{1}{2},\frac{1}{2},\frac{1}{2})$] and an energy cutoff of 45 Ry. This was done in order to check the structural and electronic properties of neutral defects as obtained with the smaller cell. Our results show minor differences between 32- and 64-atom supercell calculations verifying that the 32-atom supercell provides reliable results for the isolated N impurity in GaAs.

The formation energies of substitutional nitrogen in GaAs for a charge state q, $E_f(q)$, are calculated as a function of the chemical potentials of the constituent atoms (μ_{As}, μ_{Ga}, and μ_N) and the electron chemical potential or Fermi level (μ_e), according to the equation[13]

$$E_f(q)=E_t(q)-n_{Ga}\mu_{Ga}-n_{As}\mu_{As}-\mu_N+q(\mu_e+\epsilon_v), \quad (1)$$

where E_t is the total energy and $n_{As}(n_{Ga})$ is the number of As (Ga) atoms in the supercell. μ_e is measured with respect to the energy of the valence-band maximum ϵ_v. μ_{Ga} and μ_{As} vary over a range given by the heat of formation of GaAs. Additionally, they are constrained by the thermal equilibrium condition $\mu_{Ga}+\mu_{As}=\mu_{GaAs}$. With this condition and fixing μ_{As} and μ_N into their values at the precipitation limits ($\mu_{As[bulk]}$ and $\mu_{N[bulk]}$), in Eq. (1), we can obtain the formation energies of the N impurity in GaAs as a function of μ_e for an As-rich condition. Details about the GaAs and As bulk structure calculations can be found in Ref. 14. To calculate $\mu_{N[bulk]}$ we consider the nitrogen ground-state structure α-N_2. This structure has been successfully applied in previous calculations to characterize the upper limit of μ_N.[15]

Our results for the electronic structure of neutral defects in their minimum energy configurations are displayed schematically in Fig. 1. The wide of GaAs band gap in the figure corresponds to the theoretical value (1.23 eV). These results were obtained with the 64-atom supercell in order to minimize dispersion effects due to the supercell approach (the dispersion of the gap levels is estimated in 0.3 eV). Accord-

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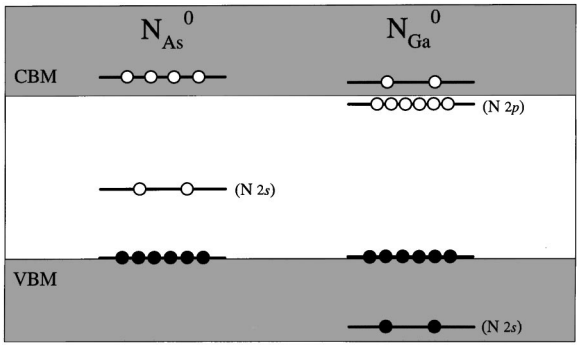

FIG. 1. Schematic representation of the single-particle energy levels in the band gap of N impurity in GaAs, in neutral charge state. The closed dots indicate electrons and the open dots indicate holes.

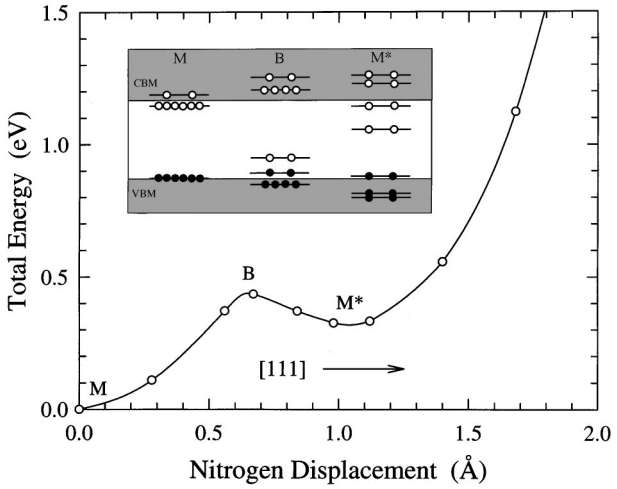

FIG. 2. Total energy as a function of the nitrogen displacement along the [111] direction of N_{Ga} in GaAs, in neutral charge state. Inserted figure displays the single-particle energy levels in the band gap for three N positions: at the minimum-energy position (M), at the top of the barrier (B) and at the metastable position (M^*).

ing to our LDA calculations, nitrogen occupying an arsenic site induces an empty nondegenerate (a_1) level in the gap at $\epsilon_v + 0.52$ eV, where ϵ_v is the top of the valence band. The wave function squared plot of this level (not shown) exhibits a strong localization around the N impurity indicating that it is the antibonding N $2s$ orbital. The corresponding bonding orbital is found about 15 eV lower in energy inside the valence band. The origin of the gap level might be associated to the strong localization of the electronic wave function at the impurity, forced by the large mismatch in size and orbital energy between the two isovalent atomic species. On the other hand, nitrogen occupying a gallium site shows an empty threefold degenerate (t_2) level in the gap at $\epsilon_v + 1.14$ eV which we identify as the antibonding N $2p$ orbital. We also find that the a_1 level associated to the antibonding N $2s$ orbital is resonant inside the valence band at $\epsilon_v - 0.59$ eV (see Fig. 1).

The equilibrium geometry of the neutral N_{As} exhibits a large inward breathing relaxation of the neighboring Ga atoms with the N–Ga bond distances of 2.07 Å, about 15% shorter than those of the unrelaxed positions, while the bond distances between first- and second-neighbor atoms (Ga–As) are ~2% larger. Similar relaxations are observed for negative charge states (1− and 2−) with a slight increase in the N–Ga bond distances (less than 1%).

The minimum energy geometry of neutral N_{Ga} shows the N atom at the Ga site preserving the T_d symmetry. The first-neighbor As atoms exhibit an inward breathing relaxation of ~11% with respect of unrelaxed positions. We also find a metastable equilibrium position with C_{3v} symmetry moving the N atom 1.1 Å from the Ga site along [111] direction, as shown in Fig. 2. The height of the barrier separating both equilibrium positions is estimated in 0.45 eV. The above structural metastability was found fixing the N atom in different positions along the [111] direction while the first-neighbor As atoms were allowed to relax. After that, the difference in total energy between the fully relaxed stable and metastable equilibrium configurations is calculated in 0.22 eV.

Inserted in Fig. 2 we show the evolution of the gap states induced by nitrogen at the minimum-energy equilibrium position (M), at the top of the barrier (B), and at the metastable equilibrium position (M^*). Previous theoretical calculations[16,17] have found a T_d–C_{3v} structural metastability for anion-antisite-like defects in GaAs (GaAs:D_{Ga}, D=P, As, and Sb). They suggest that this metastability would be an intrinsic property of III–V compounds. Our results for N_{Ga} are in good agreement with these works supporting the above suggestion.

For negative charge states, N_{Ga} shows strong off-center distortion reducing the N coordination with the addition of extra electrons. For 1− and 2− charge states, N is found threefold coordinated (with C_{3v} symmetry), while for 3− charge state it is found twofold coordinated (with C_{2v} symmetry). According to the N_{Ga} electronic structure (see Fig. 1), these distortions would be induced by the Jahn–Teller effect. However, a possible uncertainty in the highest charged system due to the small 32-atom supercell must be taken into account. The equilibrium geometry of N_{Ga} in different charge states are summarized in Table I.

We now discuss the energetics of substitutional nitrogen in GaAs in order to gain insight about the competing processes involved in the nitrogen incorporation at cation and anion sites. Figure 3 shows the formation energies as a function of the Fermi level (μ_e) for an As-rich growth condition. In the figure, the range of variation of μ_e is chosen to be the theoretical band gap, where $\mu_e = 0$ corresponds the top of the valence band (ϵ_v). In addition, the values of μ_e at which two charge states intersect indicate transition states or ionization levels.

Figure 3 shows that even for unfavorable growth conditions (As rich), N_{As} exhibits the lowest formation energies as compared with N_{Ga} being easier to be incorporated. For p-type and semi-insulating GaAs, N_{As} is found in neutral

TABLE I. Equilibrium geometry of N_{Ga} defect in GaAs in different charge states. d_{NAs} represents the mean bond distance between N and their first-neighbor As atoms and θ represents the angle between N–A bonds.

Charge	Symmetry	d_{NAs} (Å)	θ (deg)
0	T_d	2.18	109.4
1−	C_{3v}	1.99	119.3
2−	C_{3v}	2.03	119.3
3−	C_{2v}	1.83	133.9

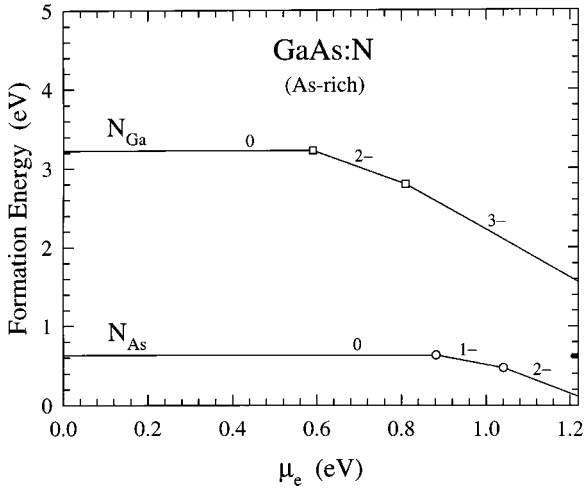

FIG. 3. Formation energies as a function of the Fermi level (μ_e) of N impurity in GaAs under As-rich conditions. The numbers on the line segments indicate charge states and the symbols indicate ionization levels.

charge state (as expected for an isoelectronic impurity), while for *n*-type GaAs it is found in negative charge states. We find two ionization levels at $\epsilon(-/0)=\epsilon_v+0.88\,\mathrm{eV}$ and $\epsilon(2-/-)=\epsilon_v+1.04\,\mathrm{eV}$. The above results suggest the existence of single and double acceptor states close to the bottom of the conduction band associated to N_{As}.

Recently, Weyers *et al.*[18] have reported PL measurements on $GaAs_{1-x}N_x$ samples for concentrations $x\leqslant 1.5\%$, which are close to that described in our calculations ($x\sim 3\%$). The most important finding in this work is the identification of a linear shift to lower energies (redshift) of the PL peak as x is increased, which is approximated by an empirical relationship ($E_{\mathrm{PL}}=E^{\mathrm{gap}}_{\mathrm{GaAs}}-12x$). We use this relation to extrapolate the corresponding PL peak for a N concentration as considered in our work ($x=0.031$), assuming our theoretical value for the GaAs band gap (1.23 eV). We find that $E_{\mathrm{PL}}=0.86\,\mathrm{eV}$, in good agreement with our result for the position of the single-acceptor $\epsilon(-/0)$ ionization energy measured with respect to valence band maximum (0.88 eV). This ionization energy can be identified as the exciton binding energy associated to the isolated N impurity according to recent theoretical calculations.[19]

In Fig. 3 we see that N_{Ga} exhibits relatively high formation energies, therefore, nitrogen occupying Ga sites is expected to occur in small concentrations. Similarly to N_{As}, N_{Ga} only exists in neutral and negative charge states also acting as acceptor. Relevant ionization levels are found at $\epsilon(2-/0)=\epsilon_v+0.59\,\mathrm{eV}$ and $\epsilon(3-/2-)=\epsilon_v+0.81\,\mathrm{eV}$. As can be seen from Fig. 3, the $1-$ charge state is never stable suggesting that N_{Ga} would form a negative-*U* center. From $(-/0)$ and $(2-/-)$ transition states with ionization levels at $\epsilon_v+0.64\,\mathrm{eV}$ and $\epsilon_v+0.55\,\mathrm{eV}$, respectively, we estimate $U=\epsilon(2-/-)-\epsilon(-/0)\approx -0.1\,\mathrm{eV}$. This unusual behavior can be associated to the nitrogen off-center distortion observed in the single negative charge state.

In summary, we have reported first-principles total-energy calculations for nitrogen substituting Ga and As atoms in GaAs. We find that both defects induce impurity-like empty levels in the band gap acting as acceptors. The midgap level of the isoelectronic N_{As} defect gives theoretical support for the experimentally observed band-edge redshift on $GaAs_{1-x}N_x$ for $x\sim 3\%$. For neutral N_{Ga} we find two equilibrium positions, a stable one with T_d symmetry and a metastable one with C_{3v} symmetry. Additionally, Jahn–Teller distortions are observed for N_{Ga} in negative charge states forming a negative-*U* center. Formation energy results suggest that the N_{Ga} defect is unlikely to occur and should be found in small concentrations instead of N_{As} which exhibits very low formation energies.

Thanks are due to A. J. R. da Silva for many helpful discussions. This work was supported by the Brazilian agencies CNPq and FAPESP. The calculations were performed at CENAPAD-SP, LNCC-RJ, and LCCA/USP.

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