Deep electronic gap levels induced by isovalent P and As impurities in GaN

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The electronic and atomic structure of isovalent substitutional P and As impurities in GaN is studied theoretically using a self-consistent plane-wave pseudopotential method. In contrast with the conventional isovalent III-V systems, GaN:P and GaN:As are shown to exhibit *deep* gap levels. The calculated donor energies are $\epsilon(1/0) = \epsilon_v + 0.22$ and $\epsilon_v + 0.41$ eV, respectively, and the double donor energies are $\epsilon(1\ 1/$

tions do not predict that these symmetry lowering relaxations ($T_d \rightarrow C_{3v}$) are energy lowering.

II. DESCRIPTION OF THE PHOTOLUMINESCENCE PROCESS VIA TOTAL ENERGIES

Our purpose is to calculate the binding energy of the impurity-bound exciton. Given the type of experimental data that are available,[17–19] we first discuss the microscopic interpretation of the measured transitions, so as to establish what needs to be calculated. Figure 1 illustrates schematically the states involved in the photoluminescence processes associated with deep centers. We depict total energies as a function of the atomic positions in the system described by a configuration coordinate Q. The lowest state $E[V^n D^m C^0]$ depicts the equilibrium ground state of the neutral defect with fully occupied valence (n electrons) and defect (m electrons) levels and with an empty conduction band. Consider now the following five-step process:

(i) Upon excitation with above-band-gap energy photons, an electron is removed from a valence band state or the impurity level to the conduction band. The energy cost of this process is depicted in Fig. 1 by $E_{\rm abs}$.

(ii) In the second stage, if the electron was excited from the valence band, the hole left behind in the valence band lowers its energy by relaxing into the defect level. At this point the system is in the excited configuration, denoted by $E[V^n D^{m\,2\,1} C^1]$ (upper parabola), corresponding to the electron in the conduction band bound to the positively charged, $m\,2\,1$ electron defect (''impurity-bound exciton'').

(iii) After the vertical electronic transition into this excited state the system relaxes via phonon emission. The Franck-Condon shift in energy associated with this process in the charged ($m\,2\,1$ electrons) defect is denoted in Fig. 1 by $E_{\rm FC}^{m\,2\,1}$.

(iv) In the relaxed excited state the system has a finite probability to make a radiative transition to the ground state, which results in the PL emission with energy $E_{\rm PL}$.

(v) Since the electronic transition is much faster than the ionic response to it, the true ground state is reached only after phonon emission ($E_{\rm FC}^{m}$). The transition energy associated with the luminescence process with *no* phonon emission is called the zero-phonon line ($E_{\rm ZPL}$).

The energy $E_{\rm ZPL}$ of the zero-phonon line can be thought of as an electronic transition where the ionic configuration can follow the electronic transition adiabatically. Therefore, $E_{\rm ZPL}$ can be determined as (Fig. 1)

$$E_{\rm ZPL} = E[V^n D^{m\,2\,1} C^1] - E[V^n D^m C^0], \tag{1}$$

where the total energies correspond to equilibrium configu-

B. Avoiding the LDA band gap error in calculating the exciton binding energy

The band gaps in LDA calculations are typically underestimated.[30] Thus, occupation of the lowest LDA conduction band in calculating the total energy of the excited state $E[V^n D^{m-1} C^1]$ [Eq. (1)] can lead to errors. We circumvent this problem by transferring the electron removed from the defect level to a uniform jellium background whose energy is the *measured* gap, rather than to the LDA conduction band (C^1) (in fact, the supercell has to be neutral in order to avoid spurious interactions between the periodic images). Due to the expected extended character of the electron wave function in the conduction band bound to the hole at the impurity site, we believe that this approximation has little effect on the actual atomic geometry in the excited configuration. Using the total energy values of the fully relaxed configurations we can calculate the zero-phonon line as

$$E_{\mathrm{ZPL}} = \{\epsilon_{\mathrm{gap}} + E[V^n D^{m-1} J^1]\} - E[V^n D^m J^0], \qquad (4)$$

where we use the *experimental* band gap value for ϵ_{gap} to avoid the LDA error, and J^1 denotes an electron in jellium. Using the definition for the exciton binding energy in Eq. (2) we find

$$E_b = E[V^n D^m J^0] - E[V^n D^{m-1} J^1]. \qquad (5)$$

Our next step is to build the connection between the thermal ionization levels and E_b. We write the total energy of defect in charge state q with respect to the total energy of the neutral defect as[31]

$$E^q_{tot} = E[V^n D^{m-q} J^q] - E[V^n D^m J^0] + q(\epsilon_v + \epsilon_F), \qquad (6)$$

where we have adopted the common practice to measure the electron Fermi energy ϵ_F with respect to the valence band maximum ϵ_v. The ionization levels $\epsilon(q,q')$ are defined as the values of ϵ_F when the total energies of two charge states become equal. In particular, writing the total energies [using Eq. (6)] for the neutral and singly positive charge states, the $(+1/0)$ ionization level is given by

$$\epsilon(+1/0) = E[V^n D^m J^0] - E[V^n D^{m-1} J^1]. \qquad (7)$$

voir formed by the uniform background charge (jellium). For this purpose, we can define ϵ

LDA calculations for V_{Zn}^{2} in ZnSe (Ref. 39) fail to reproduce the experimentally observed large Jahn-Teller relaxation.

We have thus searched for a Jahn-Teller distortion in GaN:P^{1} and GaN:As^{1}. First, we created a starting geometry corresponding to the zinc-blende structure with slight (maximum cartesian amplitude 0.25 a.u.) random displacements of all atoms. This was done in order to break possible metastable symmetric configurations. Then we let all atoms move according to the calculated quantum mechanical forces (without any symmetry constraints) until the total energy minimum was reached. The resulting bond lengths are shown in Table III. We observe a roughly one percent increase in the outward relaxation of the neighboring Ga atoms compared with the neutral charge state. Furthermore, a slight symmetry lowering relaxation (i-dependent $d^{(i)}$) is detected, which, however, cannot be decomposed into Jahn-Teller distortion exhibiting C_3

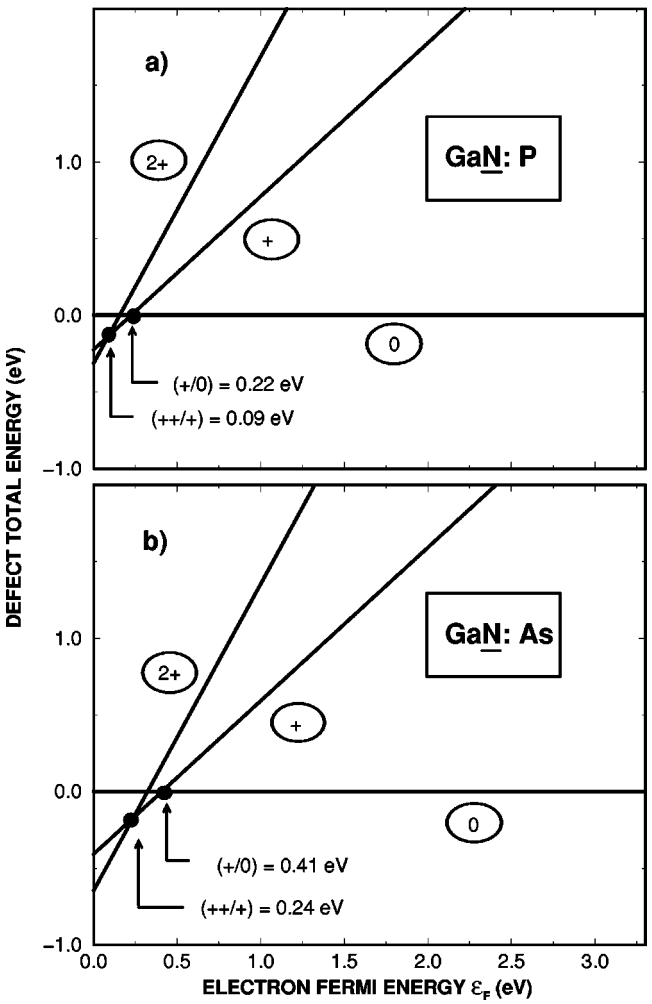

FIG. 5. Total energies of (a) GaN:P and (b) GaN:As defect in $0, 1$, and $1\ 1$ charge states as a function of the electron Fermi energy. The ionization levels are depicted with solid dots.

material.[40] The results showed that the deep states possessed very dominantly a valence band character with very little overlap with the conduction band states. This suggests that the positions (with respect to ϵ_v) of the single-particle levels found in our LDA calculations are little affected by the actual underestimate in the band gap value, and thus this band gap underestimation is not the principal factor in the difference between LDA and EPM results.

Turning to the charged defects, we find a minor splitting (a few meV) in the threefold degenerate level in the singly positive charge state, where an electron is removed from the defect level (Fig. 3). Furthermore, the single-particle levels move closer to the valence band edge as the occupancy of the level is reduced, reflecting a diminished interelectronic Coulomb repulsion.

C. Transition energies: theory and experiment

Figure 5 illustrates the total energies of GaN:P and GaN:As defects in various charge states as a function of the Fermi-level position [Eq. (6)]. The ionization levels, i.e., the Fermi-level values where the total energies of two charge states become equal [e.g., Eq. (7)], are shown as solid dots. For both defects we find the neutral, and singly and doubly positive charge states. The donor levels are found at

TABLE IV. The calculated Franck-Condon shifts for P and As impurities in GaN given by the LDA method.

Defect	E_{FC}^{m} (eV)	$E_{\mathrm{FC}}^{m\,2\,1}$ (eV)
P_N	0.08	0.06
As_N	0.11	0.09

$$\begin{aligned}
&\epsilon(1/0) = \epsilon_v + 0.22 \quad (\mathrm{GaN{:}P}),\\
&\epsilon(1/0) = \epsilon_v + 0.41 \quad (\mathrm{GaN{:}As}),\\
&\epsilon(1\ 1/1) = \epsilon_v + 0.09 \quad (\mathrm{GaN{:}P}),\\
&\epsilon(1\ 1/1) = \epsilon_v + 0.24 \quad (\mathrm{GaN{:}As}).
\end{aligned} \tag{13}$$

The recent photoluminescence experiments for P-implanted GaN by Jadwisienczak and Lozykowski[19] give the PL line at $E_{\mathrm{PL}} = 2.917$ eV, in good agreement with the results by Pankove and Hutchby[17] and Metcalfe *et al.*[18] Jadwisienczak and Lozykowski[19] have further determined the zero-phonon line to be at $E_{\mathrm{ZPL}} = 3.2709$ eV. The exciton binding energy according to Eq. (2) is thus $E_b = E_{\mathrm{gap}} - E_{\mathrm{ZPL}} = 0.232$ eV, assuming $E_{\mathrm{gap}} = 3.503$ eV as the band gap in their wurtzite samples. According to Eqs. (5) and (7) we can identify the $(1/0)$ ionization energy in our calculations as E_b. Therefore our result $E_b = 0.22$ eV [Eq. (13)] is in excellent agreement with the experimental value $E_b = 0.232$ eV.

The calculated values for the Franck-Condon shifts are shown in Table IV. Comparison of E_{FC}^{m} in the case of GaN:P to the experimental shift between the PL and ZPL (0.35 eV) shows that the calculated values are considerably smaller. On the other hand, the small Franck-Condon shifts are consistent with the relatively small atomic relaxation differences between the neutral and positive charge states described in Table III.

V. CONCLUSIONS

The self-consistent plane-wave pseudopotential calculations verify the exceptional behavior of isovalent P and As impurities in GaN: both substitutional impurities are found to induce deep levels in the band gap in contrast with all other conventional III-V systems. The defect levels are triply degenerate t_2-like orbitals primarily localized at the substitutional atom. The calculated total energies are used to estimate zero-phonon line and impurity-bound exciton binding energies associated with the photoluminescence measurements. The calculated exciton binding energy $E_b = 0.22$ eV for GaN:P is in excellent agreement with the available experimental data $E_b = 0.232$ eV.

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