Ionization energy levels in C-doped In$_x$Ga$_{1-x}$N alloys

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The In$_x$Ga$_{1-x}$N alloys present levels as a result of the intentional (doped) or unintentional (contamination) introduction of C atoms into the host semiconductor. The III-V nitride semiconductors and their alloys usually crystallize in the wurtzite structure although the zinc blende structure has also been grown. We obtained the In$_x$Ga$_{1-x}$N:C ionization energies from first-principles calculations of the two ordered wurtzite and zinc blende structures using different exchange and correlation terms. In accordance with the experimental results, the ionization levels could give rise, on some occasions, to a metallic impurity band.

III-V nitride semiconductors and their alloys have attracted much attention in recent years as a result of their great potential for technological applications. In the wurtzite structure (Ws), AlN, GaN, and InN have direct energy band gaps, a high melting point, a high thermal conductivity, and a large bulk modulus. These properties can be used for short wavelength light-emitting diodes (LEDs), laser diodes, optical detectors, high-frequency devices, etc. Remarkable progress has been made in methods for growing, thus increasing the crystal quality of these materials. In particular, the ternary III-V semiconductor compound In$_x$Ga$_{1-x}$N is one candidate as the active layer for both blue emission and white LEDs because its band gap may vary from 0.7 to 1.1 eV (InN) and 3.5 eV (GaN) depending on the In concentration. InN is expected to be a suitable material for electronic devices such as high mobility transistors because of its small effective mass compared to other nitrides. However, InN has not had so much attention as GaN because of the difficulty in growing single crystalline InN. The difficulty results from a low InN dissociation temperature. Because of the thermal instability of InN, the growth of good quality In$_x$Ga$_{1-x}$N films with a high In content is difficult. This is primarily because the lattice mismatch is very large, especially for GaN and InN. Their thermal expansion coefficients are also different.

For the manufacture of devices, it is also essential to be able to introduce p- and n-type doping in a controlled manner. This implies the introduction of dopant impurities, which produce deep localized acceptor or donor impurity states. The group-IV elements Si and Ge have been traditionally used in semiconductor technology for many years as dopant elements in AlN and GaN. On the other hand, C has recently been used to obtain p-type conductivity in the GaN with the zinc blende structure (ZBs).[1] Carbon contamination is usually unavoidable during the growth of group-III nitrides.[2–5] At low concentrations C enters into N-vacancies, producing a marked improvement in the crystalline properties of the material.[6] Understanding the electronic properties of these impurities in the In$_x$Ga$_{1-x}$N lattice is of fundamental importance for achieving useful doping.

Group-III nitrides usually crystallize in Ws. Most of the experimental and theoretical work for In$_x$Ga$_{1-x}$N has been carried out on the Ws and with x close to zero. The ZBs is only slightly higher in energy (10 meV per two-atom unit[7]). Thus, the Ws and the ZBs may coexist, although in different proportions, depending on the experimental growth conditions.

In this paper we research the ionization energies (IEs) induced by the incorporation of C into substitutional sites of the In$_x$Ga$_{1-x}$N for ZBs and Ws, by analyzing the two substitutions: C by N (C$_N$) and C by Ga (C$_{Ga}$).

In order to obtain the donor (e_D), acceptor (e_A), and gap energies, we used total-energy differences[8,9] instead of single-particle energies (equivalent to using Koopman's theorem) since correlation problems and systematic errors[8] are decreased. The formation energy of a defect or impurity in the charge state q is[10]

$$\Delta H_f(\mu_e;q) = E(q) - E_H(0) - \sum_i n_i \mu_i + q\mu_e = E(q)$$
$$- E(0) + q\mu_e, \qquad (1)$$

where $E(q)$ and $E_H(q)$ are the total energies from a supercell calculation with (In$_x$Ga$_{1-x}$N:C) and without (In$_x$Ga$_{1-x}$N) a defect or impurity, μ_e is the electron chemical potential (Fermi energy), n_i indicates the number of atoms of type i (host or impurity atoms) that have been added to ($n_i>0$) or removed from ($n_i<0$) the solid when the defect or impurity is created, and μ_i are the corresponding chemical potentials of these species. The IEs are the values of the electron chemical potential at which charge states change. Therefore, $e_D=E(0)-E(+1)$ and $e_A=E(-1)-E(0)$. For the host VB edge, we take the ionization energy $e_V=E_H(0)-E_H(+1)$ and the electron affinity $e_C=E_H(-1)-E_H(0)$ for the CB edge. The resulting gap $E_g=E_H(-1)-2E_H(0)+E_H(+1)$ is closer to the experimental than the estimate from the single-particle eigenvalues.

In order to obtain the total energies needed to obtain the IEs, we use the density-functional theory. The standard Kohn–Sham[11] (KS) equations are solved self-consistently.[12] The local spin density (LDA) and generalized gradient (GGA) approximations are used for the exchange-correlation energy. The LDA with the Perdew–Zunger parametrization
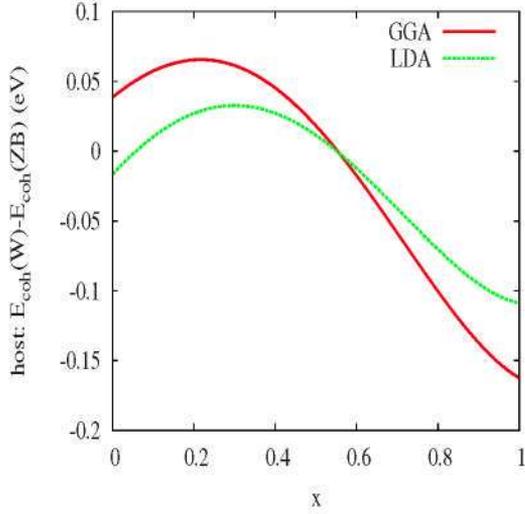
FIG. 1. (Color online) Difference between the energies of the Ws and the ZBs as a function of x with both GGA and LDA.

to the Ceperley–Alder numerical data,[13] and the GGA in the form of Perdew, Burke, and Ernzerhof.[14] The standard Troullier–Martins[15] pseudopotentials are adopted and expressed in the Kleinman–Bylander[16] factorization. The valence wave functions are expanded in a numerically localized pseudoatomic orbital basis set.[17] A double-zeta with polarization basis set has been used for all atoms. The dimension of the k point grid varies with the cell size in order to keep a constant k point density in the Brillouin zone.

In order to study the $In_xGa_{1-x}N$ alloys, we have used a large number of ordered ZBs and Ws with varying In compositions. For the Ws, we have used 32- and 108-atom supercells. For the ZBs, we have used 54-, 64-, and 216-atom supercells. Theoretical results[18,19] indicate that the equilibrium lattice constant c in the Ws shows a linear variation versus x, but the lattice parameter a shows a slight deviation from that calculated in the linear interpolation of the binaries. Nevertheless, this slight deviation has almost no influence on the calculated IEs. Therefore, for both the ZBs and the Ws, we have used the lattice parameters from the linear interpolation of the binaries.

When the Ga atoms are replaced by In atoms, the number of nonequivalent structures is large. Experimentally, the results indicate a good homogeneity[20] of these alloys. Therefore, we have used the most homogeneous structures for the calculations. Other nonequivalent local structures for some concentrations have been analyzed in the literature.[19,21]

First, we have obtained the energy difference between the Ws and the ZBs as a function of x, with both GGA and LDA (Fig. 1). The energy differences are small, between 6 and 16 meV depending on x. These results are in accordance with the results in the literature[7] of 10 meV per two-atom unit reference. Thus, the Ws and the ZBs could coexist and will be analyzed in this work.

Figure 2 and 3 show the variation of the e_D, e_A, and CB (e_C) edge with the concentration x of $In_xGa_{1-x}N$:C alloys for the two substitutions and two exchange-correlation functionals. These energies have been referenced to the VB (e_V) edge, i.e., $e_V = 0$ and $E_g = e_C$. When the M atom (N or Ga) is substituted by C, the charge state is neutral (C_M^0). The e_D and e_A correspond to the C_M^{1+}/C_M^0 and C_M^0/C_M^{1-} transformations, respectively. Therefore, the μ_e energy range where the
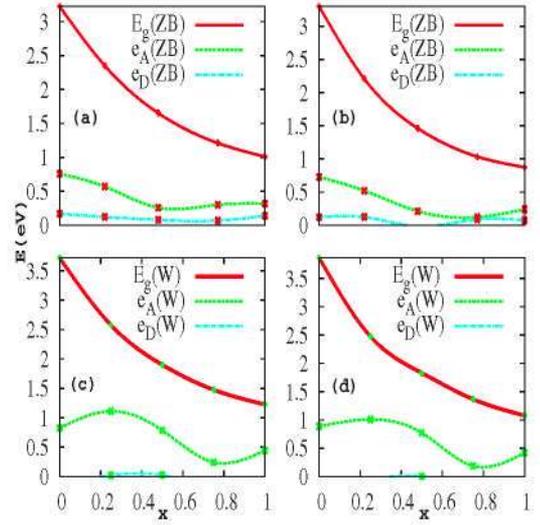

FIG. 2. (Color online) e_D, e_A and gap ($E_g = e_C$) energies for the C_N substitution in $In_xGa_{1-x}N$ as a function of x for both the ZBs (panels a and b) and Ws (panels c and d), and with both, GGA (panels a and c), and LDA (panels b and d). The VB edge (e_V) has been chosen as zero energy.

charge state C_M^0 is stable is between e_D and e_A in Figs. 2 and 3. The C_M^{1+} and C_M^{1-} charge states are stable when μ_e is below e_D and above e_A, respectively.

The experimental gaps for the GaN at the Ws and at the ZBs are 3.41–3.55 eV (Refs. 22 and 23) and 3.21–3.45 eV (Refs. 22 and 24), respectively. The experimental gap currently accepted for the InN at the Ws is 0.7–1.1 eV.[25] These experimental values compare well with our results for $x=0$ and $x=1$, respectively, in Figs. 2 and 3.

For the C_N substitution in GaN, the IEs reported experimentally in the literature with respect to the VB edge are $e_A = 0.215$,[1] 0.23,[5] and 0.86 eV.[26] Some of the values obtained from theoretical studies are $e_A = 0.2$ eV (Ws),[27] 0.37 eV,[28] 0.26 eV (Ref. 29) (ZBs), 0.80 eV (Ws),[30] and $e_D = 0.16$ eV (ZBs).[29] The results in Fig. 2 for the e_A with $x=0$ are within the range of experimental and other theoretical results. For the ZBs the e_D is also very close to the VB, in accordance with Ref. 29.
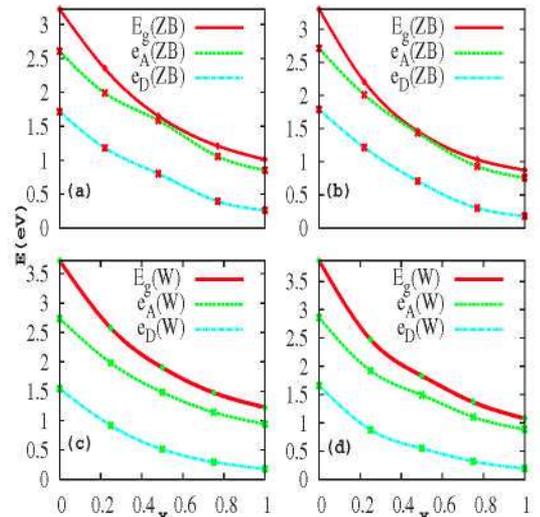

FIG. 3. (Color online) The same legend as in Fig. 2, but for the C_{Ga} substitution.

Carbon could, in principle, behave as a donor when incorporated into the Ga site (C_{Ga} substitution). Nevertheless, the formation energy for this configuration is much larger than for the incorporation of carbon into the N site, where it acts as an acceptor.[8,29] A reason of this large formation energy is that C and N have similar atomic radii, while the substitution of the much larger Ga induces a large lattice strain energy of a few eV.[27] The e_A and e_D for the C_{Ga} substitution into the ZBs from theoretical results[29] are e_A = 1.90 eV and e_D = 1.85 eV, respectively. Nevertheless the gap obtained in this reference is 2.03 eV. The result for the e_D (Fig. 3) is 1.7–1.8 eV, whereas the e_A is 2.6–2.8 eV. The latter result is larger than Ref. 29 (1.90 eV). Nevertheless the gap obtained in this reference is 2.03 eV, whereas the gaps of this work are very close to the experimental gaps for both structures: ZBs and Ws.

The low temperature Hall data for p-GaN (ZBs) (Ref. 31) suggests the existence of a metallic impurity band separated from the VB. The Hall coefficient and resistivity for n-InN (ZBs) and $In_xGa_{1-x}N$ (mix of ZBs and Ws) for larger temperatures show metallic conduction.[31] Therefore, for the InN and the $In_xGa_{1-x}N$, the impurity band is merged with the VB and the conduction is very similar to what one should expect for metals. It is consistent with the very high n-type conductivity of the films and with the results of this work. For small x, the e_A is more separated from the VB, whereas with the increase in x, the level is closer to the VB. This level, with the increase in the impurity concentration, could lead to the impurity band.

In summary, we report the results of first-principles total-energy calculations for e_D and e_A of C-doped $In_xGa_{1-x}N$ alloys and the gaps of the host semiconductor. Our results, with a wide range of x, compare GGA and LDA. Both the Ws and the ZBs are analyzed using several supercell sizes. The results are well compared for the x values where there are theoretical or experimental results. These results could be useful for the analysis of samples where the two phases coexist.

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