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Computational study of the effect of Al and In on the formation energies and acceptor levels of Mg and C dopants in GaN

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Abstract

The effect of aluminium and indium on the formation energies and acceptor levels of magnesium and carbon dopants in GaN have been calculated using a density functional approach. Single aluminium and indium atoms are incorporated into the lattice at a minimal distance from the acceptor species. The formation energies are obtained as a function of the position of the Fermi level. In the absence of aluminium or indium, magnesium in a charge neutral state is found to have a formation energy of 1.1 eV, whereas carbon has a formation energy of 2.6 eV. In the presence of indium, the magnesium formation energy rises to 1.4 eV, whereas the addition of aluminium has no effect. For carbon, the presence of aluminium and indium increases the formation energy by 0.4 and 0.3 eV, respectively. Furthermore, the calculations predict that the magnesium acceptor level becomes more shallow by the addition of aluminium (from 0.14 to 0.01 eV above the valence band maximum), but is made deeper by indium (from 0.14 to 0.27 eV above the valence band maximum). The carbon acceptor level is found to remain approximately unchanged with aluminium and indium doping. These results are compared to experimental data and the effect of various approximations in the calculations is discussed.

1. Introduction

It is well known that obtaining higher electrical conductivity in p-type GaN is important for improving device performance. This is difficult to achieve, however, due to the high binding energy of acceptor species, which leads to low acceptor doping efficiencies. For example, the acceptor levels in GaN are typically around a factor of ten deeper than the corresponding acceptor levels found in GaAs. The most commonly used acceptor species is magnesium which, when substituted on the gallium site, introduces an acceptor level at around 200 meV

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above the valence band maximum [1], although other values have been reported that vary from 130 meV [2] to 290 meV [3]. Given the depth of 200 meV the electrical activation at room temperature is only 6%. The problem of low activation is exacerbated by compensation effects caused by donor species (as-grown GaN is inherently n-type) and by passivation of the acceptor by hydrogen. Typically, doping concentrations of 10^{19} cm^{-3} are required, which lead to hole densities of the order of 10^{17} cm^{-3}. One approach has been to simply dope with higher concentrations of magnesium. However, attempts to increase doping concentrations beyond 10^{19} cm^{-3} are found not to increase the hole density because of self-compensation effects. Higher magnesium concentrations also lead to an unwanted luminescence peak centred at 2.8 eV, which is caused by a deep donor (probably the nitrogen vacancy) to magnesium acceptor recombination [4].

Recent progress has been made by employing AlGaN superlattices consisting of GaN wells and AlGaN barriers [5, 6]. Such superlattices introduce modulations in the position of the valence band maximum across the structure. This in turn produces spatial fluctuations in the position of the acceptor level. A strong enhancement (up to tenfold) of the acceptor activation is achieved due to the acceptor energy levels in the barrier being energetically close to the valence band states in the wells. Despite this success, the use of AlGaN superlattices has the major disadvantage of introducing conduction band carriers which impede the electron transport.

Qualities desired in an acceptor species include good solubility (i.e. low formation energy), stability against compensation and a small activation energy. In this paper, formation energies and acceptor levels are calculated for magnesium and carbon acceptors. Since InGaN and AlGaN are commonly used in GaN devices we also investigate the influence of aluminium and indium in order to determine whether these dopants can improve the properties of the acceptors.

2. Computational method

The calculations are based on density functional theory in the local density approximation (LDA) and employ norm conserving non-local pseudopotentials. Electron wave functions are expanded in terms of a plane wave basis set and the electronic ground state is reached using a conjugate gradients minimization scheme, as implemented by the computer code CETEP [7]. The d electrons are included as valence electrons for GaN in order to reproduce the correct lattice parameters and an accurate c/a ratio. A computational cell of 108 atoms is used in which the atomic coordinates are also relaxed using conjugate gradients. This cell contained 12 (0001) layers each containing nine atoms and was approximately $9.5 \times 9.5 \times 15.2$ Å^3 in size. For k-point sampling we use the gamma point only and the cutoff energy for the plane wave basis is 800 eV. Test calculations on small cells show that the computed lattice parameters and the c/a ratio agree with experimental values to within 0.1%. To obtain the magnesium and carbon acceptor levels and formation energies, a magnesium atom is substituted on a gallium site and a carbon atom is substituted on a nitrogen site. To study the influence of aluminium and indium on these acceptor levels and energies, single aluminium and indium atoms are incorporated into the supercells at a minimal distance from the acceptor species. The substitution of single atoms into the supercells leads to the formation of $In_{0.02}Ga_{0.98}N$ and $Al_{0.02}Ga_{0.98}N$ alloys. As aluminium and indium are substitutional on the gallium site they only form second nearest neighbours to magnesium, but can form nearest neighbours to carbon.

Acceptor levels for magnesium and carbon are calculated using the formation energy formalism which is commonly employed in density functional studies to obtain defect levels. Following Neugebauer and Van de Walle [8], the defect formation energy for a general impurity

or defect is given by

$$E^f(q) = E^{tot}(q) - \sum_A n_A \mu_A - q(\varepsilon_v + E_F) \tag{1}$$

where n_A is the number of atoms of species A and μ_A is the chemical potential of species A. $E^{tot}(q)$ is the total energy of the cell for charge state q and E_F is the electron chemical potential or Fermi level which is measured with respect to the valence band maximum ε_v. The chemical potentials define the reservoir from which the atoms are taken from or brought to in order to create the defect. Both gallium and nitrogen are in thermal equilibrium with GaN and therefore the gallium and nitrogen chemical potentials are not independent but are related by

$$\mu_{Ga} + \mu_N = \mu_{GaN(bulk)}. \tag{2}$$

The chemical potentials must also obey certain boundary conditions. For example, μ_{Ga} must be less than the chemical potential found in bulk gallium, otherwise gallium metal would form in preference to binding with nitrogen. Likewise, μ_N must be less than the chemical potential in a nitrogen molecule. The formation energy depends on the growth conditions. For example, impurities which are substitutional on the gallium site will have the highest formation energy under gallium-rich conditions and impurities which are substitutional on the nitrogen site will have the highest formation energies under nitrogen-rich conditions. These growth conditions are determined by the gallium and nitrogen chemical potentials. The gallium-rich limit corresponds to $\mu_{Ga} = \mu_{Ga(bulk)}$ and the nitrogen-rich condition corresponds to $\mu_N = \mu_{N(molecule)}$.

As can be seen from (1) the formation energy for charge states depends on the position of the valence band maximum. However, for an impurity-containing supercell ε_v is not so straightforward to determine. The value required is the position of the single particle valence band maximum eigenvalue for an isolated defect surrounded by an infinite solid. The value obtained using a supercell, where the defect is necessarily located within an array of defects, may deviate significantly from the desired value due to induced distortions of the band structure by the defect [9]. Often ε_v is taken as the single particle valence band maximum eigenvalue at the gamma point in GaN. Mattila and Zunger [10] provide a means of finding ε_v in the defect-containing supercell by calculating the average effective potential. In the present work this alignment procedure is carried out following an alternative method which has been shown to provide the same results [11]. The potential alignment is found by noting the shift in energy of lower lying gallium s and p bands in the defect-containing supercell compared with the same bands in a bulk GaN supercell. The value for the valence band maximum is then taken to be ε_v as found in bulk GaN, corrected by the band shift. Typical values for this band shift are +0.04 eV and therefore this correction can significantly influence the transition energy results.

It is noted also that for charge states the total energy of the supercell is shifted with respect to the energy of a neutral charge supercell. In fact the supercell must not contain any net charge, otherwise the electrostatic energy per supercell would be divergent. This problem is overcome in the calculations by adding a uniform background charge to the cell ('jellium') with density $n = -q/V_c$, where V_c is the volume of the cell and q is the charge state. This background charge cancels the divergence but also introduces additional fictitious interactions, which causes the shift in the total energy. The total energy obtained for a charge state must therefore be corrected before the formation energy is calculated.

The total correction which should be made has been discussed by Shah [12] and the result (for a cubic supercell) is simply stated here. This result includes corrections which account for electrostatic defect–defect interactions as well as interactions between the defect charge and the neutralizing background charge [13]. In making such a correction the convergence of the

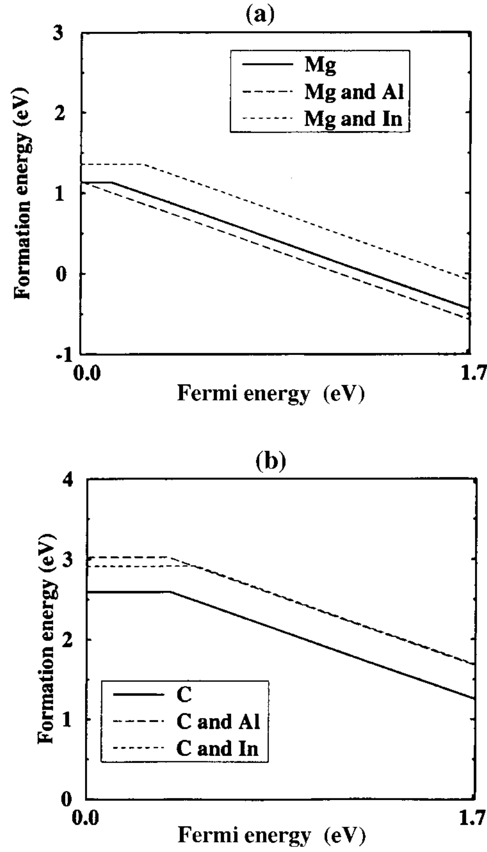

Figure 1. Defect formation energy of (a) Mg_{Ga}, Mg_{Ga} with aluminium and Mg_{Ga} with indium for the neutral and singly negative charge states, (b) C_N, C_N with aluminium and C_N with indium for the neutral and singly negative charge states.

total energy of a charged supercell with respect to system size can be significantly improved. The corrected energy is given by

$$E = E_0 - q\langle\phi_0\rangle - \frac{\alpha q^2}{2L} + \frac{2\pi q}{3V_c}\int_\Omega \rho_1(r)r^2\,\mathrm{d}^3r + \frac{1}{2}\int_{r'\notin\Omega}\int_{r\in\Omega}\frac{\rho_1(r')\rho_d(r)}{|r'-r|}\,\mathrm{d}^3r'\,\mathrm{d}^3r \tag{3}$$

where ρ_d is the local distortion of the bulk charge density induced by the defect and ρ_1 is ρ_d made neutral by subtracting a point charge from it. Ω denotes the supercell, L is the length of the supercell and $\langle\phi_0\rangle$ is the average potential of the bulk material. All of the terms on the right-hand side of (3) become zero in the limit of an infinite size supercell except for the first two: E_0 and $-q$ multiplied by the average potential. In this work the average potential is obtained by plotting the total energy of a bulk GaN supercell (108 atoms) as a function of the charge state. The value of $\langle\phi_0\rangle$ obtained from the slope of this plot is found to be -9.88 eV. The third and subsequent terms in (3) are not, in this work, used to correct the total energy of supercells in charge states. Therefore the formation energy obtained is that of a defect located within an infinite array of defects rather than the formation energy of a perfectly isolated defect.

3. Results and discussion

Figure 1 shows the formation energy of magnesium and carbon acceptors as a function of the position of the Fermi level. The results were obtained under gallium-rich conditions and the chemical potentials of magnesium and carbon were determined from separate calculations on the bulk elements. The chemical potentials of indium and aluminium were found from calculations on InN and AlN, respectively. In figure 1 the full curve illustrates the case where no aluminium or indium is present. Each curve is composed of two parts, one horizontal part corresponding to the charge neutral defect and a second part with a negative slope corresponding to the defect in a singly negative charge state. The formation energy of the two charge states becomes equal at the intersection of the two parts and indicates an ionization energy corresponding to an acceptor level. For most Fermi level positions the dopants adopt a singly negative charge state and thus act as single acceptors. The magnesium acceptor level is found to be at $\varepsilon_v + 0.14$ eV. This is some 0.06 eV lower than the most commonly reported experimental result as well as the level obtained using density functional theory by Neugebauer and Van de Walle [14]. However, it is noted that the most recent experimental evidence suggests a shallow level of 0.13–0.15 eV above the valence band maximum [15]. The carbon acceptor level is calculated to be $\varepsilon_v + 0.37$ eV. Thus C_N is found to be deeper (by 0.23 eV) than the computed magnesium level. The agreement with experimental results is difficult to gauge as the computed C_N level is deeper than some experimental values but shallower than others. For example, Fischer *et al* [16] report a value of $\varepsilon_v + 0.23$ eV for the C_N acceptor level, while Strite [17] reports a value of $\varepsilon_v + 0.86$ eV. Previous DFT studies report a value of $\varepsilon_v + 0.2$ eV [18]. However, the deep acceptor level is in agreement with the general result that the activation efficiency of carbon is significantly less than that of magnesium. For example, recent studies on the optical activation behaviour of ion implanted acceptors estimate the activation efficiency of carbon to be some 50 times worse than that of magnesium [19]. A low formation energy of 1.1 eV is found for Mg_{Ga} for a neutral charge whereas C_N is found to have a higher formation energy of 2.6 eV. Thus Mg_{Ga} is predicted to have greater solubility than C_N.

We now consider the influence of aluminium and indium both on the formation energy and the depth of the acceptor level. For both magnesium and carbon the addition of aluminium and indium to the lattice in near neighbour sites has a small effect on the formation energy. For example, the nearby indium atom slightly raises the Mg_{Ga} formation energy (for the charge neutral site) from 1.1 to 1.4 eV, whereas the addition of aluminium is found to have no effect. For C_N the presence of nearest-neighbour aluminium and indium increases the formation energy by 0.4 and 0.3 eV, respectively.

Concerning the depth of the magnesium level, the calculations predict the level becomes more shallow with the addition of aluminium (from 0.14 to 0.01 eV above the valence band maximum), but is made deeper by indium (from 0.14 eV to 0.27 eV above the valence band maximum)—see figure 1. Thus, according to these results, doping with aluminium should significantly improve the efficiency of magnesium doping, whereas indium should have the opposite effect. Unfortunately this is difficult to reconcile with experimental results for which the activation energy for magnesium acceptors increases in $Al_xGa_{1-x}N$ alloys but decreases in $In_xGa_{1-x}N$ alloys [20, 21]. In these studies the aluminium composition studied ranged from $x = 0.05$ to $x = 0.33$ and the indium composition ranged from $x = 0.05$ to $x = 0.15$. These composition ranges are a little larger than those studied computationally. The carbon acceptor level is found to remain approximately unchanged with aluminium and indium doping. The depth of the level is not at all affected by aluminium, whereas for indium a small increase from 0.37 to 0.48 eV above the valence band maximum is found.

We note in conclusion that it may be too ambitious to calculate such changes in the positions of acceptor levels using the current methodology. Uncertainties in the energies can arise during the band alignment procedure and also from the correction made to the total energy for the case of charge states. In addition, the doping levels studied here are somewhat smaller than those investigated experimentally and we have also assumed that aluminium and indium are nearest (or next-nearest) neighbours to the magnesium and carbon acceptors. Further calculations are in progress to improve the accuracy of the total energy and to study a larger range of aluminium and indium compositions and configurations. However, the formation energies of magnesium and carbon acceptors, as well as the change in formation energy upon doping with indium and aluminium, are reliable in the current work and conclusions can be drawn from these. For example, carbon is found to have a higher formation energy than magnesium and the introduction of 2% indium and aluminium into nearby lattice sites has little effect on the acceptor formation energy.

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References

[1] Orton J W 1995 *Semicond. Sci. Technol.* **10** 101
[2] Seghier D and Gislason H P 1999 *Physica* B **273–274** 46
[3] Rubin M, Newman N, Chan J S, Fu T C and Ross J T 1994 *Appl. Phys. Lett.* **64** 64
[4] Kaufmann U, Kunzer M, Maier M, Obloh H, Ramakrishnan A, Santic B and Sclotter P 1998 *Appl. Phys. Lett.* **72** 1326
[5] Schubert E F, Grieshaber W and Goepfert I D 1996 *Appl. Phys. Lett.* **69** 3737
[6] Kozody P, Hanson M, DenBaars S P and Mishra U K 1999 *Appl. Phys. Lett.* **74** 3681
[7] Payne M C, Teter M P, Allan D C, Arias T A and Joannopoulos J D 1992 *Rev. Mod. Phys.* **64** 1045
[8] Neugebauer J and Van de Walle C G 1996 *Festkorperprobleme—Adv. Solid State Phys.* **35** 25
[9] Garcia A and Northrup J E 1991 *Phys. Rev. Lett.* **74** 1131
[10] Mattila T and Zunger A 1998 *Phys. Rev.* B **58** 1367
[11] Lento J 2000 Private communication
[12] Shah R 1996 *PhD Thesis* University of Cambridge, ch 4
[13] Makov G and Payne M C 1995 *Phys. Rev.* B **51** 4014
[14] Neugebauer J and Van de Walle C G 1996 *Appl. Phys. Lett.* **68** 1829
[15] Kim D J, Ryu D Y, Bojarczuk N A, Karasnski J, Guha S, Lee S H and Lee J H 2000 *J. Appl. Phys.* **88** 2564
[16] Fischer S, Wetzel C, Haller E E and Meyer B K 1995 *Appl. Phys. Lett.* **67** 1298
[17] Sřite S C 1994 *Properties of Group III Nitrides (EMIS Datareview series 11)* ed J H Edgar (London: INSPEC) p 272
[18] Boguslawski P and Bernholc J 1997 *Phys. Rev.* B **56** 9496
[19] Skromme B J and Martinez G L 2000 *Mater. Res. Soc. Proc.* **595** W9.8
[20] Kumakura K, Makimoto T and Kobayashi N 2000 *Japan. J. Appl. Phys.* **39** L337
[21] Katsuragawa M, Sota S, Komori M, Anbe C, Takeuchi T, Saki H, Amano H and Akasaki I 1998 *J. Cryst. Growth* **190** 528