A8.1 Native defects, impurities and doping in GaN and related compounds: general remarks

C.G. Van de Walle, J. Neugebauer and C. Stampfl

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A INTRODUCTION

Controlled introduction of impurities forms the basis of much of semiconductor technology; indeed p-type (acceptor-doped) and n-type (donor-doped) layers and the junctions between them control carrier confinement, carrier flow and ultimately the device characteristics. Achieving both n-type and p-type conductivity has traditionally proved to be a challenge in wide-bandgap semiconductors.

The doping can be affected by native defects such as vacancies (V_{Ga} and V_N), self-interstitials (Ga_i and N_i) and antisites (Ga_N and N_{Ga}). Such defects may cause self-compensation, e.g. when one tries to dope the material p-type, certain native defects which act as donors may spontaneously form and compensate the deliberately introduced acceptors. In GaN, a specific native defect was long believed to play an even more important role: the nitrogen vacancy, which acts as a donor, was thought to occur in large concentrations, thereby causing unintentional n-type conductivity.

Great progress has been made in recent years in our understanding of impurities and native defects in the nitrides: the availability of higher-quality epitaxial layers has allowed for better experiments, and first-principles calculations have provided a comprehensive theoretical foundation. A discussion of our current understanding of native defects is given in Datareview A8.2. In this Datareview we provide a framework for discussing incorporation of defects and impurities, and then focus on donor and acceptor impurities.

B FORMATION ENERGIES

The equilibrium concentration of an impurity or native defect is given by

$$c = N_{sites} \exp^{-E^f / k_B T} \quad (1)$$

where E^f is the formation energy, N_{sites} is the number of sites the defect or impurity can be incorporated on, k_B is the Boltzmann constant and T is the temperature. EQN (1) shows that defects with a high formation energy will occur in low concentrations.

The formation energy is not a constant but depends on the growth conditions. For example, the formation energy of an oxygen donor is determined by the relative abundance of O, Ga and N atoms, as expressed by the chemical potentials μ_O, μ_{Ga} and μ_N, respectively. If the O donor is charged (as is expected when it has donated its electron), the formation energy depends further on the Fermi level (E_F), which acts as a reservoir for electrons. Forming a substitutional O donor requires the removal of one N atom and the addition of one O atom; the formation energy is therefore:

$$E^f(GaN:O^q_N) = E_{tot}(GaN:O^q_N) - E_{tot}(GaN,bulk) - \mu_O + \mu_N + qE_F \quad (2)$$

First-principles calculations allow explicit derivation of $E_{tot}(GaN:O^q_N)$, the total energy derived for a system containing substitutional O on an N site. q is the charge state of the O donor. Similar expressions apply to other impurities and to the various native defects. The state-of-the-art first-

principles calculations used to derive E_{tot} in EQN (2) do not require any adjustable parameters or any input from experiment. The computations are founded on density-functional theory, using a supercell geometry and ab initio pseudopotentials. Details of the computational approach can be found in [1-4].

In principle, the free energy should be used in EQN (1). Use of the (zero-temperature) formation energy as defined in EQN (2) implies that contributions from vibrational entropy are neglected. Explicit calculations of such entropies are very demanding, and currently not feasible for the large number of defects to be addressed. These entropy contributions cancel to some extent, e.g. when solubilities are calculated; in general, they are small enough not to affect qualitative conclusions.

The assumption of equilibrium which is implicit in EQN (1) is expected to be satisfied at the high temperatures at which metal-organic chemical vapour deposition (MOCVD) growth of nitrides is carried out. At lower temperatures, such as those used in molecular-beam epitaxy (MBE), deviations from equilibrium may occur.

The Fermi level E_F is not an independent parameter, but is determined by the condition of charge neutrality. In principle equations such as EQN (2) can be formulated for every native defect and impurity in the material; the complete problem (including free-carrier concentrations in valence and conduction bands) can then be solved self-consistently, imposing charge neutrality. However, it is instructive to plot formation energies as a function of E_F in order to examine the behaviour of defects and impurities when the doping level changes. For clarity of presentation the atomic chemical potentials may be set equal to fixed values; a general case can always be addressed by referring back to EQN (2). The fixed values used in the figures shown below correspond to Ga-rich conditions ($\mu_{Ga} = \mu_{Ga(bulk)}$), and to maximum incorporation of the various impurities, with solubilities determined by equilibrium with Ga_2O_3, Si_3N_4 and Mg_3N_2.

C DONOR IMPURITIES

n-type doping of GaN has always proved to be quite easy: the material exhibits a tendency to be n-type conductive if no special precautions are taken. This was long thought to be caused by the spontaneous formation of nitrogen vacancies. It is now known (see Datareview A8.2) that nitrogen vacancies are unlikely to form in n-type material. The observed n-type conductivity must therefore be attributed to unintentional incorporation of dopant impurities [5].

FIGURE 1 summarises first-principles results for native defects and impurities relevant for n-type doping. It is clear that O and Si have much lower formation energies than V_N; these impurities can be readily incorporated in n-type GaN. Both O and Si form shallow donors in GaN. The slope of the lines in FIGURE 1 indicates the charge state of the defect or impurity (see EQN (2)): Si_{Ga}, O_N and V_N all appear with slope +1, indicating single donors. Oxygen has been proposed as a potential source of n-type conductivity in GaN as early as 1983 [6,7]. A host of recent experiments have confirmed that unintentionally doped n-type GaN samples contain Si or O concentrations consistent with the observed electron concentrations [8-10].

C1 DX Centres

Oxygen-doped material exhibits a freezeout of carriers when it is subjected to hydrostatic pressure exceeding 20 GPa [11,12]. This behaviour is explained by a 'DX-like' behaviour of the oxygen donor. The prototype DX centre is Si in GaAs, which undergoes a transition from a shallow to a deep centre when hydrostatic pressure is applied [13]. First-principles calculations for oxygen in GaN under pressure [12] show that at sufficiently high pressure the oxygen impurity moves off the substitutional site and assumes an off-centre configuration: a large outward relaxation introduces a deep level in the bandgap. Silicon donors do not exhibit this transition [11,12].

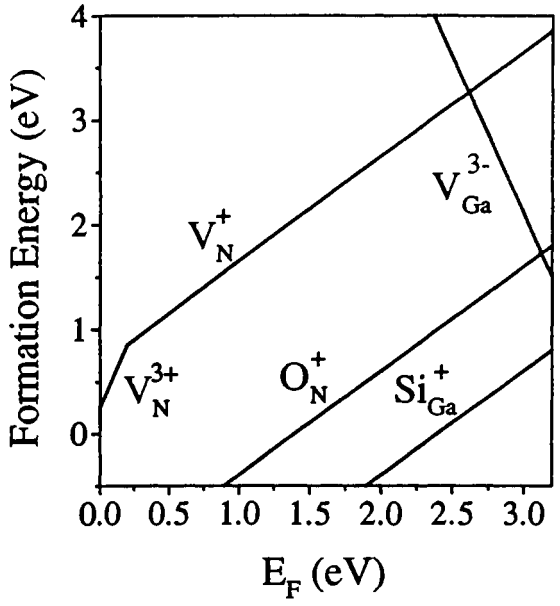

FIGURE 1 Formation energy as a function of Fermi energy for dominant native defects (nitrogen and gallium vacancies) and donors (oxygen and silicon) in GaN. The zero of Fermi energy is located at the top of the valence band.

C2 n-Type Doping of $Al_xGa_{1-x}N$

Alloying with AlN increases the bandgap similarly to the application of hydrostatic pressure; the behaviour of impurities in AlGaN should therefore be similar to that in GaN under pressure. First-principles calculations [12,14] predict a DX transition for oxygen in $Al_xGa_{1-x}N$ when $x > 0.3$, consistent with the observed decrease in n-type conductivity of unintentionally doped $Al_xGa_{1-x}N$ [15,16]. Once again, Si donors do not exhibit the DX transition [12,16]. Interestingly, the DX transition does not occur in zincblende AlGaN [12].

C3 Compensation

FIGURE 1 shows that gallium vacancies (V^{3-}_{Ga}) have relatively low formation energies in highly doped n-type material (E_F high in the gap); they could therefore act as compensating centres. Yi and Wessels [17] have reported evidence of compensation by a triply charged defect in Se-doped GaN. Gallium vacancies have also been proposed to be responsible for the 'yellow luminescence' (YL) in GaN. Yellow luminescence is discussed in Datareview A8.7.

Even though Si does not exhibit the DX transition, n-type doping of $Al_xGa_{1-x}N$ with high Al content will be hampered due to compensation by cation vacancies, which act as triple acceptors, as discussed in Datareview A8.2.

D ACCEPTOR IMPURITIES

Magnesium has emerged as the p-type dopant of choice. Still, p-type doping levels in GaN and AlGaN alloys are lower than desirable for low-resistance cladding layers and ohmic contacts. Achieving higher hole concentrations with Mg as the dopant has proved difficult: even though it is possible to increase the Mg concentration, the hole concentration levels off and even decreases past a certain point [18]. First-principles investigations [19] have revealed that the most important factor is the solubility of Mg in GaN, which is limited by competition between incorporation of Mg acceptors and formation of Mg_3N_2. Mg prefers the substitutional Ga site, and incorporation of Mg on substitutional N sites (Mg_N) or on interstitial sites (Mg_i) is unfavourable, as seen in FIGURE 2.

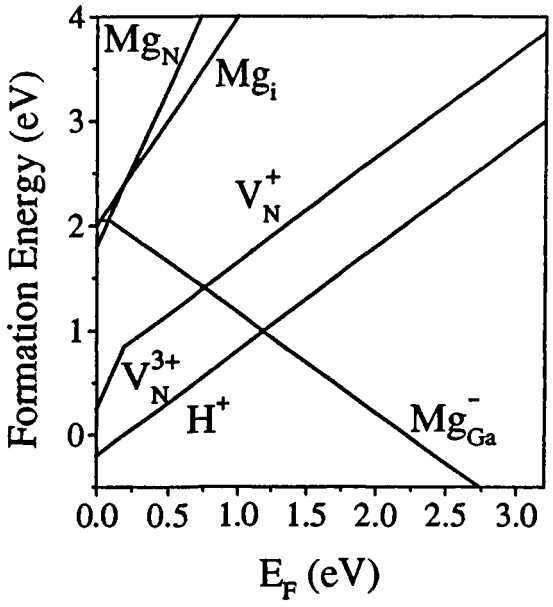

FIGURE 2 Formation energy as a function of Fermi energy for Mg in different configurations (Ga-substitutional, N-substitutional and interstitial configuration). Also included are the native defects (nitrogen vacancies) and interstitial H.

D1 Effect of Hydrogen on p-Type Doping

Hydrogen has strong effects on the properties of p-type GaN. A detailed discussion is given in Datareview A8.8.

D2 Compensation

The nitrogen vacancy, which had a high formation energy in n-type GaN (see FIGURE 1), has a significantly lower formation energy in p-type material, and acts as a compensating centre. The suppression of compensation by vacancies in the presence of hydrogen is discussed in Datareview A8.8. FIGURE 2 shows that V_N can occur in a 3+ as well as a + charge state; the +/3+ transition is characterised by a large lattice relaxation [2]. Compensation by V_N may therefore be responsible for the observed persistent photoconductivity effects [20,21]. The nitrogen vacancy also may give rise to the blue lines (around 2.9 eV) commonly observed by photoluminescence in Mg-doped GaN [14,21].

D3 p-Type Doping of $Al_xGa_{1-x}N$

The efficiency of Mg doping has been observed to decrease rapidly with increasing Al content x in $Al_xGa_{1-x}N$ [22]. Magnesium has no tendency to form deep levels (so called AX levels, analogous to DX for donors) [14], thus ruling out a shallow-deep transition as the source of the drop in hole concentration. Calculations of the Mg acceptor indicate that its ionisation energy is higher in AlN (0.4 eV) than in GaN (0.2 eV) [23]. This increase in the ionisation energy leads to a decrease in doping efficiency. Compensation by native defects is another important mechanism contributing to the decline in hole concentrations. As discussed in Datareview A8.2, two defects with low formation energies may inhibit successful p-type doping of $Al_xGa_{1-x}N$, namely the nitrogen vacancy and the cation interstitial. The nitrogen vacancy has a strikingly lower formation energy in AlN than in GaN. Compensation by nitrogen vacancies is the likely cause of the decreased doping efficiency of Mg when the Al content is raised in $Al_xGa_{1-x}N$ alloys. The cation interstitial has a low formation energy in zincblende material, but is much higher in energy in wurtzite.

D4 Alternative Acceptors

The performance of an acceptor can be judged on the basis of three main criteria: (i) solubility; (ii) stability against compensation by other configurations of the acceptor dopant (e.g. interstitials); and (iii) depth of the acceptor level (ionisation energy). Each of these aspects can be addressed on the basis of results obtained from first-principles calculations. The solubility of a substitutional acceptor corresponds to the equilibrium concentration of the impurity in the lattice, which is determined by the formation energy. The formation energy of the impurity in configurations other than the substitutional site determines the likelihood of incorporation on those sites. Interstitial configurations tend to be favourable for elements with a small atomic radius, such as Li or Be.

Extensive theoretical investigations [24,25] have not produced any candidate with characteristics exceeding those of Mg in all respects. The only acceptor with solubility comparable to Mg, and a potentially smaller ionisation energy, is Be. However, Be may suffer from compensation by Be interstitials which act as donors. Be has been reported to produce high p-type conductivity in cubic GaN [26].

D5 Compensation due to Foreign Impurities

Avoiding oxygen contamination during growth of p-type GaN is essential. The oxygen formation energy shown in FIGURE 1 clearly extrapolates to very low values in p-type GaN. Any oxygen present in the growth system will therefore be readily incorporated during p-type growth.

E CONCLUSION

Specific results for donor and acceptor doping have been reviewed. The main conclusions for n-type GaN are that (i) nitrogen vacancies are not responsible for unintentional n-type conductivity; (ii) background n-type doping is caused by unintentional incorporation of Si and O donors; and (iii) oxygen (but not silicon) behaves as a DX centre in GaN under pressure and in AlGaN alloys. For p-type GaN we conclude that (i) Mg is still the acceptor of choice; (ii) the resulting hole concentration is limited due to Mg solubility; (iii) incorporation of Mg on interstitial sites or antisites is not a problem; and (iv) compensation by nitrogen vacancies may occur.

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