

THEORY OF POINT DEFECTS AND COMPLEXES IN GaN

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ABSTRACT

We have studied the electronic and energetic properties of native defects, impurities and complexes in GaN applying state-of-the-art first-principles calculations. An analysis of the numerical results gives direct insight into defect concentrations and impurity solubility with respect to growth parameters (temperature, chemical potentials) and into the mechanisms limiting the doping levels in GaN. We show how compensation and passivation by native defects or impurities, solubility issues, and incorporation of dopants on other sites influence the acceptor doping levels. The role of hydrogen in enhancing the *p*-type doping is explained in detail. We also discuss the mechanisms responsible for the experimentally observed limitation of the free-carrier concentration in *p*-type GaN.

INTRODUCTION

During the past few years interest in GaN-based devices has grown rapidly, stimulated by the accomplishment of bright, highly-efficient green/blue light-emitting diodes [1]. However, despite the progress in devices, doping problems remain an important issue. Current doping levels are sufficient for producing light-emitting diodes, but the lack of high *p*-type doping levels may be a major obstacle in achieving III-V nitride laser diodes. Native defects are often invoked to explain the shortcomings in doping.

With the advent of increasingly fast computers and methodical improvements, first-principles calculations have evolved into a powerful tool to study various properties of defects and impurities in semiconductors. With the capability to calculate accurate total energies and electronic structure, it became possible to investigate the character and the position of defect levels, the atomic structure of the defect, as well as the energy to create the defect. More recently, formalisms have been developed to use the total energy of the defect to calculate defect concentrations, under the assumption of thermodynamic equilibrium [2, 3]. The same formalism can also be extended to the calculation of impurity solubilities [4, 5].

In the present paper we will give an overview about theoretical results for native defects and impurities in GaN. We will mainly focus on the problem of acceptor doping limits in GaN, particularly for Mg, which is presently the acceptor of choice to obtain *p*-type conductivity. However, hole concentrations are still lower than desired. We therefore discuss various mechanisms which may limit the hole concentration: compensation by native defects and impurities, solubility limits, and incorporation of the Mg acceptor on other sites. The role of hydrogen, in particular its ability to enhance the *p*-type doping, is discussed in detail.

FORMALISM

The equilibrium concentration c of an impurity or defect at temperature T is determined by its formation energy, E^f :

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

where N_{sites} is the number of sites the defect can be built in. g is a degeneracy factor representing the number of possible configurations in which a defect can be formed on the *same* site. k_B is the Boltzmann constant and S the vibrational entropy. The vibrational entropy is, at the present stage of our work, not explicitly included, which would be computationally very demanding. Entropy contributions cancel to some extent [6], and are small enough not to affect any qualitative conclusions. The effect of entropy can be included in an approximate way; experimental and theoretical results show that the entropy S is typically in the range between 0 (no entropy contributions) and $10 k_B$ (where k_B is the Boltzmann constant) [7].

The formation energy depends on various parameters. For example, the formation energy of a Mg acceptor is determined by the relative abundance of Mg, Ga, and N atoms. In a thermodynamic context these abundances are described by the chemical potentials μ_{Mg} , μ_{Ga} , and μ_{N} . If the Mg acceptor is charged, the formation energy depends further on the Fermi level (E_F), which acts as a reservoir for electrons. Forming a substitutional Mg acceptor requires the removal of one Ga atom and the addition of one Mg atom; the formation energy is therefore:

$$E^f(\text{GaN:Mg}_{\text{Ga}}^q) = E_{\text{tot}}(\text{GaN:Mg}_{\text{Ga}}^q) - \mu_{\text{Mg}} + \mu_{\text{Ga}} + qE_F \quad (2)$$

where $E_{\text{tot}}(\text{GaN:Mg}_{\text{Ga}}^q)$ is the total energy derived from a calculation for substitutional Mg, and q is the charge state of the Mg acceptor. Similar expressions apply to the hydrogen impurity, and to the various native defects. For calculating the total energies we have performed first-principles calculations based on density-functional theory (DFT) using a supercell approach with 32 atoms per cell, a plane-wave basis set with 60 Ry cutoff and soft Troullier-Martins pseudopotentials [8]. Details of the method and convergence checks can be found elsewhere [9, 10, 11].

NATIVE DEFECTS

We have calculated the position of the defect levels and the formation energies for all native defects in GaN: vacancies (V_{Ga} , V_{N}), antisites (Ga_{N} , N_{Ga}), and interstitials (Ga_i , N_i). All relevant charge states were taken into account. The positions of the defect levels corresponding to the neutral charge state are shown in Fig. 1. From these results we can immediately classify the defects into donors, acceptors and amphoteric defects: V_{N} and Ga_i are donors, V_{Ga} is an acceptor, and N_i and both antisites are amphoteric.

We find that antisites and interstitials have high formation energies, and are therefore very unlikely to occur in any significant concentration [11]. The vacancies, however, have lower formation energies. Under conditions of thermodynamic equilibrium, low formation energies are required for the defect to occur in high concentration. In particular, the nitrogen vacancy (a single donor) has a low formation energy under *p*-type and semiinsulating conditions, and the Ga vacancy (a triple acceptor) gets a low formation energy under *n*-type conditions. Thus, based on the assumption of thermodynamic equilibrium, the dominant

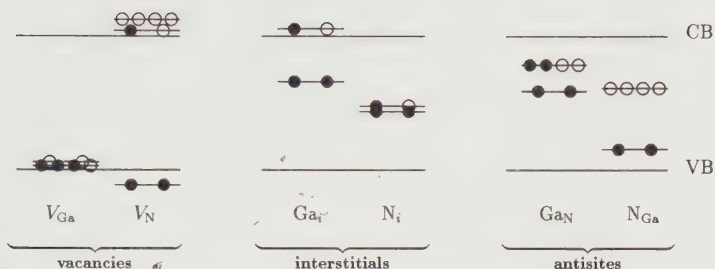


Figure 1: Schematic representation of the defect levels in GaN. The occupations are shown for the neutral charge state; filled circles indicate electrons, open circles indicate holes.

native defects are the vacancies: in *p*-type GaN the N vacancy, in *n*-type GaN the Ga vacancy.

Based on Eq. (1) the defect concentration as a function of temperature can be calculated. The results are shown in Fig. 2, where we have assumed Ga-rich conditions (which appear to be common in experimental growth conditions). For this calculation undoped GaN is assumed; no impurities are included. It is important to note that the defect concentrations are not independent from each other: they are coupled via the condition of charge neutrality. The total charge associated with electrons in the conduction band, holes in the valence band, and charges on the defects must be zero [7].

Figure 2 shows that for all growth temperatures the N vacancy is the defect with the highest concentration in undoped GaN. The concentration of Ga vacancies is orders of magnitude smaller, and the other native defects occur only in insignificant concentrations. Generally, the defect concentration increases with increasing temperature. However, even at growth temperatures as high as 1300 K [typical for metalorganic vapor deposition (MOCVD)] the N vacancy concentration is orders of magnitude too small to explain the high unintentional carrier concentrations of $10^{18} \dots 10^{20} \text{ cm}^{-3}$ found in “autodoped” GaN samples.

We have proposed two alternative explanations for the high unintentional carrier concentration. First, we stress that our conclusions about N vacancies applies to *isolated point defects*. A vacancy-related defect or extended defect may be involved, if it acts as a donor. Second, we propose unintentional incorporation of donor impurities. In particular, we find Si and O to have a high solubility in GaN; our calculations also show that C can be excluded as a possible donor [12]. Recent progress has enabled the growth of GaN with low unintentional carrier concentrations ($10^{16} \dots 10^{17} \text{ cm}^{-3}$), and even semiinsulating GaN has been reported.

ATOMIC AND MOLECULAR HYDROGEN IN GaN

Hydrogen is a common impurity in many semiconductors, and well known for its ability

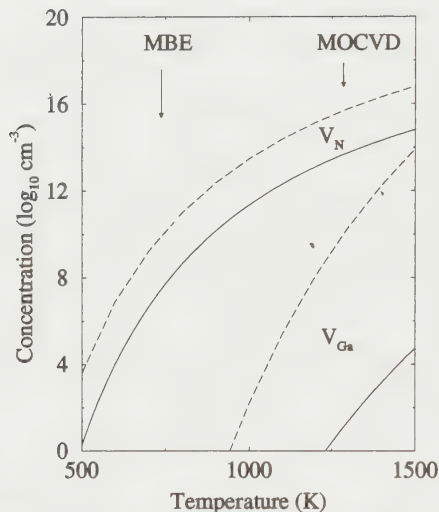


Figure 2: Equilibrium concentration of native defects in undoped GaN versus growth temperature. Ga-rich conditions are assumed. Lower (solid line; $S = 1k_B$) and upper limit (dashed line; $S = 10k_B$) are shown.

to terminate dangling bonds, passivate or compensate both shallow and deep defects, and to induce extended defects [13]. In modern high-temperature growth techniques such as MOCVD and HVPE (hydride vapor phase epitaxy), which are used to grow high-quality epitaxial GaN, hydrogen is highly abundant. There is also strong experimental evidence that hydrogen is involved in the passivation of acceptors in GaN [14].

We have recently investigated energetics and migration behavior of monatomic H and H molecules in GaN. The main results regarding the energetics of interstitial H in GaN are summarized in Fig. 3, which displays the formation energy for the different charge states of H (H^+ , H^0 , H^-) as a function of the Fermi level. For this plot, we assumed that the H chemical potential μ_H is fixed at the energy of a free H atom, as a reference. In p -type GaN, H^+ has the lowest formation energy, indicating that H acts as a donor. For n -type GaN, H^- has the lowest formation energy: H acts as an acceptor. From these results we can conclude that: (i) H is not a dopant but (ii) it may compensate both acceptors and donors.

From Fig. 3 we further derive that the solubility of p -type GaN is considerably higher under p -type conditions than under n -type conditions. We also found that the migration barrier for diffusion of H^+ is low, while the barrier of diffusion of H^- is high [15]. Our theoretical predictions were very recently confirmed by experimental observations of Götz and Johnson [16] on plasma hydrogenation of MOCVD-grown GaN: H is readily incorporated in p -type GaN, consistent with a high diffusivity and solubility, whereas no detectable levels

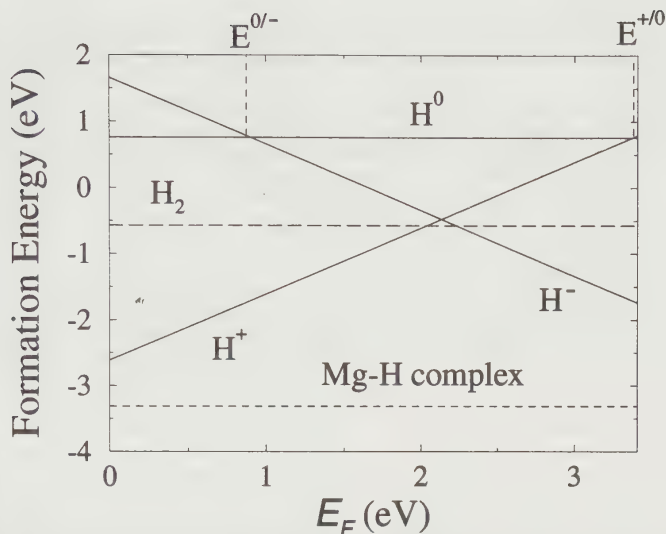


Figure 3: Formation energy as a function of the Fermi level for H^+ , H^0 and H^- (solid lines), for a hydrogen molecule (dashed line), and for a magnesium-hydrogen complex (long-dashed line). The formation energy is referenced to the energy of a free H atom.

of H were found in *n*-type GaN, consistent with a low diffusivity as well as lower solubility.

The fact that the neutral charge state is never stable is characteristic for a “negative- U ” system. The value of U is given by the difference between the $+/0$ and $0/-$ transition levels: $U = E^{0/-} - E^{+/0} \approx -2.4$ eV. A negative- U behavior appears to be common for H in semiconductors; it was also found for H in Si and GaAs. However, the value found here for GaN is unusually large, and, to the best of our knowledge, larger than any predicted or measured value for any defect in any semiconductor.

We have also studied hydrogen molecules in GaN. The formation energy and atomic geometry were calculated for several symmetric as well as asymmetric configurations. The formation energies for all the calculated structures are nearly degenerate; the value for the energetically most stable configuration is included in Fig. 3. We have also investigated the H_2^+ geometry, proposed by Chang and Chadi [17], where one H is located at the bond-center site and the other at either the N or Ga antibonding site. Our calculations show that these configurations are energetically even less favorable than those where the H atoms may form a H-H bond. As shown in Fig. 3, H_2 is unstable with respect to dissociation into monatomic H. The formation energy of ≈ -0.6 eV is much higher than that of H_2 in vacuum (-2.4 eV). Both properties, the unfavorably high formation energy and the low stability of the H_2 molecule are distinctly different from the behavior of H in Si and GaAs.

DOPING LIMITS OF Mg-DOPED GaN

Magnesium is the most commonly used acceptor in GaN; it has an ionization energy of ≈ 0.16 eV [18] and can be incorporated in concentrations up to $\approx 10^{20}$ cm $^{-3}$. However, the relatively deep character of the Mg acceptor level implies that only a tiny fraction of the Mg acceptors will be ionized, explaining why the maximum achievable hole concentration is much smaller than the Mg concentration. Several procedures are conceivable to overcome this problem: (i) use of acceptors with a lower ionization energy and (ii) an increase of the acceptor concentration. In the past, several other acceptor impurities were studied, but Mg was found to be the most shallow acceptor [19]. However, even if an acceptor with a smaller binding energy exists, the question is whether it can be incorporated in sufficiently high concentrations.

We will therefore discuss in detail what the doping-limiting mechanisms are for Mg in GaN. The conclusions we draw can be applied also to other acceptors. The doping level can be limited by three mechanisms: (i) solubility issues, (ii) compensation or passivation by native defects and impurities, and (iii) incorporation of the dopant on sites where it no longer acts as an acceptor. In the following discussion we will show that these mechanisms cannot be treated independently, but the achievable hole concentration depends on a combination of these effects.

Solubility

The formation energy to create a Mg_{Ga} acceptor can be separated into two independent processes: (i) the removal of a Ga atom (creation of a Ga vacancy) and (ii) the chemisorption of a Mg atom on this site. For both processes the energy depends on the specific growth conditions which are characterized by the chemical potentials. The removed Ga atom has to be brought to a reservoir for Ga atoms where it has the energy μ_{Ga} . If this energy is high (Ga-rich environment) the formation energy will be high as well. The same argumentation can be applied to the incorporation of Mg; the formation energy depends thus on two external parameters (μ_{Ga} , μ_{Mg}). An upper limit for the Mg chemical potential is the formation of bulk Mg. Our calculations show that an even more stable configuration is Mg₃N₂, having a large cohesive energy of 4.8 eV. The chemical potentials then have to obey the relation:

$$2\mu_{Mg} + 3\mu_{Ga} = \mu_{Mg_3N_2} \quad (3)$$

The formation of Mg₃N₂ is thus an *upper limit* for the solubility of Mg in GaN, giving at the same time a *lower limit* for the Mg_{Ga} formation energy.

The formation of Mg₃N₂ or Mg precipitates may be suppressed by working far away from thermodynamic equilibrium, i.e., at low temperatures. This may work for MBE (molecular beam epitaxy) growth (where low temperatures are characteristic), however, we expect that the temperatures in MOCVD and related growth methods ($T > 1000$ K) are high enough to realize thermodynamic equilibrium.

Compensation by native defects

The incorporation of acceptors dramatically changes the position of the Fermi level causing strong changes in the formation energies of native defects and impurities. Defects that are very high in energy under semiinsulating or *n*-type conditions (and thus occur

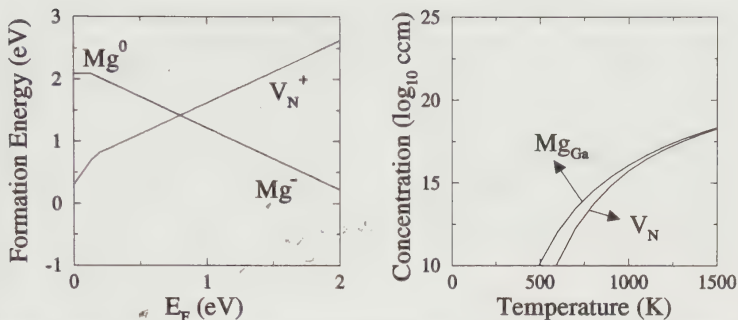


Figure 4: Formation energy vs. Fermi level for the Mg_{Ga} acceptor and the native defects. The corresponding equilibrium concentrations are given in (b). Ga-rich conditions are assumed.

only in small concentrations) may now become energetically favorable. In *p*-type GaN, as discussed in the Section about native defects, the N vacancy (a donor) is the defect with the lowest formation energy. Figure 4(a) shows the calculated formation energies for the native defects and the Mg_{Ga} acceptor under Ga-rich conditions. For the calculation of the Mg_{Ga} formation energy the limited solubility of Mg in GaN [Eq. 3] was taken into account, which gives a lower limit for the formation energy. The position of the kink in the Mg formation energy at ≈ 0.2 eV gives the position of the acceptor level, close to the experimental value (0.16 eV) [18].

Using the calculated formation energies, and taking into account that the Fermi energy is not a free parameter but fixed by the condition of charge neutrality, the equilibrium defect concentration [Eq. 1] for each defect can be calculated as function of temperature [3]. The results, displayed in Fig. 4(b), show that the Mg concentration, as expected, increases with the growth temperature. The only native defect which occurs in relevant concentrations is the N vacancy. At temperatures exceeding 1000 K the Mg acceptors become increasingly compensated by the N vacancies. Compensation by native defects is therefore *potentially* a major concern for high-temperature growth techniques. Growth at low temperatures as characteristic for MBE may suffer less from this problem since non-equilibrium conditions probably apply. This may explain why *p*-type GaN without post-growth treatment was successful in MBE [20, 21].

Role of hydrogen in achieving *p*-type doping in GaN

Until recently, efforts to dope GaN *p*-type led to highly-resistive material. It was not until 1989 that Amano *et al.* made a major breakthrough when they observed that initially compensated Mg-doped GaN can be activated by low-energy electron beam irradiation (LEEBI) [22]. Nakamura later showed that the Mg activation can be achieved equally well by thermal annealing at 700°C under N_2 ambient [14]. Nakamura further observed that the process was reversible, with *p*-type GaN reverting to semiinsulating when annealed in a NH_3

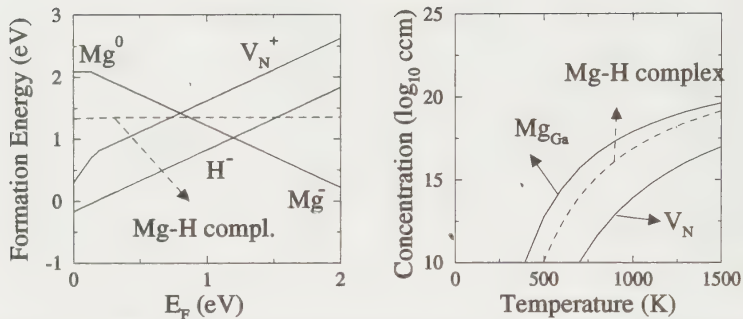


Figure 5: Formation energy vs. Fermi level for the Mg_{Ga} acceptor and the neutral Mg-H complex. Also included are the native defects and interstitial H. The corresponding equilibrium concentrations are given in (b) as a function of the growth temperature. H rich conditions are assumed.

ambient [14], revealing the crucial role played by hydrogen. Based on these observations, Van Vechten *et al.* [23] proposed a model describing acceptor passivation by H in which Mg-H defect complexes are converted to active Mg acceptor impurities by LEEBI. This model highlights the important role of H, but leaves various issues unanswered, such as why activation can be achieved also by thermal annealing, the lack of H incorporation in *n*-type GaN, and the success of *p*-type doping without post-growth treatments in MBE.

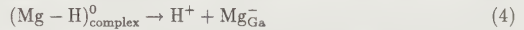
We will now combine our results about native defects, interstitial hydrogen and Mg acceptors to address these questions. Figure 5(a) displays the formation energies as a function of the Fermi level. In addition, the formation energy of the neutral Mg-H complex is included, which will be discussed later in detail. Figure 5(a) shows that for all Fermi energies H is energetically more favorable than the dominant native defect, the N vacancy. From the calculated formation energies the equilibrium concentrations for all defects can be calculated. The results, displayed in Fig. 5(b), reveal a remarkably different behavior compared to the H-free limit (Fig. 4): the Mg concentration is *increased* and the N vacancy concentration is *decreased*. Both effects are beneficial for doping. We further find that the Mg and H concentrations are virtually identical indicating that H completely compensates the Mg acceptors. At the growth temperature, the concentration of Mg-H complexes is orders of magnitude smaller than isolated (but compensated) Mg_{Ga} . Our finding of virtually complete compensation of the Mg acceptors is consistent with the experimental observations: the only cases where *p*-type GaN has been achieved without any post-growth treatment involved MBE growth where H is absent. MOCVD-grown Mg doped GaN (where H is highly abundant) is compensated and highly resistive.

Let us now describe the beneficial role of H on the Mg incorporation in GaN in a more qualitative way. In Fig. 5(a) the Fermi level can be roughly estimated to be near the crossing point between the acceptor and the dominant donor species. At this point their formation energies, and hence their concentrations, are equal, ensuring charge neutrality. This approximation works well if the Fermi level is far enough from the valence-band edge;

free carriers can then be neglected. If only native defects are present (H-free case), the N vacancy is the dominant defect, and the crossing occurs at about ≈ 0.8 eV. If H is present, the crossing point and thus the Fermi energy shifts to higher energies, resulting in a *decrease* of the acceptor (Mg) formation energy and an *increase* of the donor (N vacancy) energy. Consequently, a lowered defect concentration and an increased acceptor concentration is achieved.

In order to study the interaction between Mg and H in more detail we have calculated the complete total-energy surface for a H atom around a Mg_{Ga} acceptor [15]. We find that Mg and H form a neutral complex with an atomic structure very different from the well established acceptor-hydrogen complexes in other semiconductors (where a bond center (BC) configuration is preferred): The H prefers the (antibonding) AB site of one of the N neighbors around the Mg atom.

Our calculated binding energy for the neutral Mg-H complex with respect to its dissociation



is $E_b \approx 0.7$ eV [15], the positive binding energy indicating that the formation of Mg-H complexes is energetically favorable. If the formation of Mg-H complexes is energetically favorable, why then is the concentration of isolated Mg and H atoms larger than the concentration of complexes [see Fig. 5(b)]? The reason is the large difference in the configurational entropy between a point defect and a complex. As pointed out above, the condition of charge neutrality ensures that the formation energies of the acceptor (Mg) and the dominant donor (H) are almost equal; let us call this energy $E_{\text{defect}} = E_f^{\text{Mg}} = E_f^{\text{H}}$. The complex formation energy is then given by $E_{\text{compl}} = 2E_{\text{defect}} - E_b$. The prefactor in the equilibrium concentration [Eq. (1)] depends on the number of possible configurations, which is for a point defect the number of either Ga or N atoms (N_{sites}). For the Mg-H complex it is the number of Ga sites (the location of the Mg atom) times the degeneracy factor g indicating the number of possible orientations of the Mg-H complex, which is four; indeed, the H atom can bond to each of the four N atoms surrounding the Mg atom. The concentrations for the defect and the complex are then given by:

$$c_{\text{defect}} = N_{\text{sites}} \exp(-E_{\text{defect}}/k_B T) \quad (5)$$

$$c_{\text{complex}} = N_{\text{sites}} g \exp(-E_{\text{compl}}/k_B T) \quad (6)$$

If we neglect the degeneracy factor the ratio between complex concentration and the concentration of the isolated defects depends solely on the difference in formation energy: for $E_{\text{compl}} < E_{\text{defect}}$ (which is equivalent to $E_{\text{defect}} < E_b$) the complex formation dominates, otherwise dissociation is predominant. Thus, complex formation is the dominant mechanism (and controls the achievable concentration of the dopants) only if the energy gain due to complex formation is larger than the energy necessary to create either one of the constituents.

For the specific choice of chemical potentials made here, the complex binding energy is not large enough to prevent dissociation of the Mg-H complex during growth. However, the Mg and H will form pairs when the sample is cooled to room temperature, consistent with experimental observations [16]. The beneficial character of H incorporation is thus not due to complex formation, but simply due to compensation. Complexes are formed only after growth and do not affect the achievable acceptor concentration.

In order to activate the Mg, post-growth treatments are necessary. The first step in the activation process is the dissociation of the Mg-H complex. Our calculated dissociation

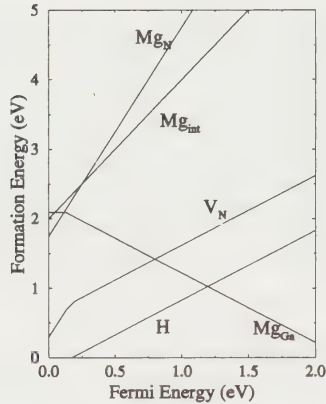


Figure 6: Formation energy as a function of the Fermi level for Mg in different configurations (Mg_{Ga} , Mg_{I} , Mg_{N}). Also included are the native defects and interstitial H.

barrier is ≈ 1.5 eV, which should be considered a lower limit: only a jump to a nearest neighbor site has been considered in this calculation, and the attractive electrostatic interaction between the negative Mg acceptor and the positive H atom may slightly increase this value. This barrier is low enough to be overcome at modest annealing temperatures (around 300°C). Experimental results show, however, that activation has to be carried out at much higher temperatures ($> 600^\circ\text{C}$) [14]. The reason is that dissociation alone is insufficient; in order to prevent the H from compensating the Mg acceptor it has to be either removed (to the surface or into the substrate) or neutralized (e.g., at an extended defect). This phenomenon is well known from studies of complex dissociation in Si; activation can be achieved at much lower temperatures if an electric field is applied which sweeps the H out of the region [24].

Incorporation of Mg on other sites

Another mechanism, that may limit the hole concentration, is self-compensation of the Mg acceptors: instead of being incorporated on the Ga substitutional site the Mg may be built in on other sites where it is electrically inactive or even becomes a donor. As possible configurations we have investigated the N substitutional site (Mg_{N}) and several interstitial configurations.

The calculated formation energies are displayed in Fig. 6. The positive slope in the formation energy indicates that Mg in both configurations acts as a donor: Mg, as a double donor, Mg_{N} as a triple donor. Whereas the behavior of Mg_{I} is expected, the donor character for Mg_{N} is not as obvious: at first sight Mg should act as a triple acceptor. The replacement of the “small” N atom ($r_{\text{cov}} = 0.75 \text{ \AA}$) with a “large” Mg atom ($r_{\text{cov}} = 1.36 \text{ \AA}$) results in a large increase of the nearest neighbor bond length (by 24% !), giving rise to substantial changes in the positions of the defect levels. The large strain around the Mg atom further explains the high formation energy, rendering this site energetically unfavorable.

Figure 6 shows that the formation energies of Mg_i and Mg_N become comparable with Mg_Ga only under extreme p -type conditions. We further find that the N vacancy or hydrogen (if present), are the dominant donors: their formation energies are lower for *all* Fermi energies. We therefore conclude that Mg will always prefer the Ga substitutional site: incorporation on other sites can be ruled out. For other possible acceptors (particularly elements with a small ionic radius), the situation may be different.

CONCLUSIONS

Based on first-principles calculations we have studied several mechanisms which may limit the hole concentration in Mg-doped GaN. Two mechanisms are found to be important: (i) the formation of Mg_3N_2 precipitates (solubility limit) and (ii) the compensation by native defects. Incorporation of the Mg atoms on the N site or in an interstitial configuration was found to be negligible. Combining our numerical results about native defects, interstitial H and the Mg impurity we could identify why H incorporation increases the acceptor concentration and simultaneously reduces compensation by native defects. An analysis of these results reveals that this mechanism should also work for other *acceptors* in GaN. However, it is by no means general: it does not work for donor impurities in GaN and may fail for other wide-band-gap semiconductors.

ACKNOWLEDGMENTS

This work was supported in part by ARPA. One of the authors (J.N.) acknowledges financial support by the DAAD (German Academic Exchange Service).

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