PROPERTIES, PROCESSING AND APPLICATIONS OF

Gallium Nitride and Related Semiconductors

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

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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

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

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:

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

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].

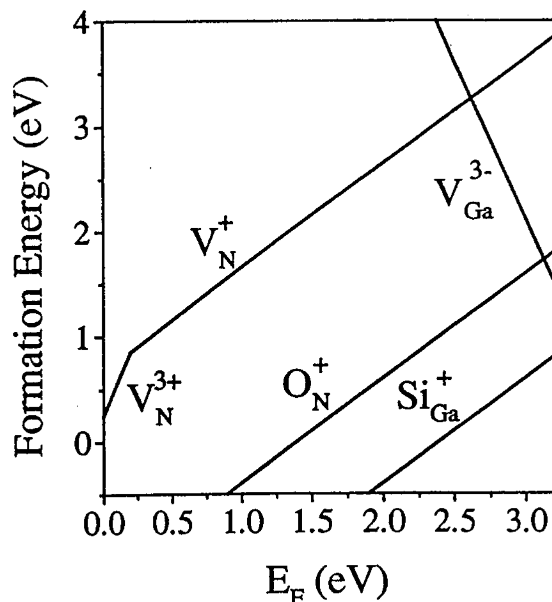

FIGURE 1 Formation energy as a function of Fermi energy for dominant native defects (nitrogen and gallium vacancies) and donors (oxygen and silicon) in GaN. The zero of Fermi energy is located at the top of the valence band.

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.

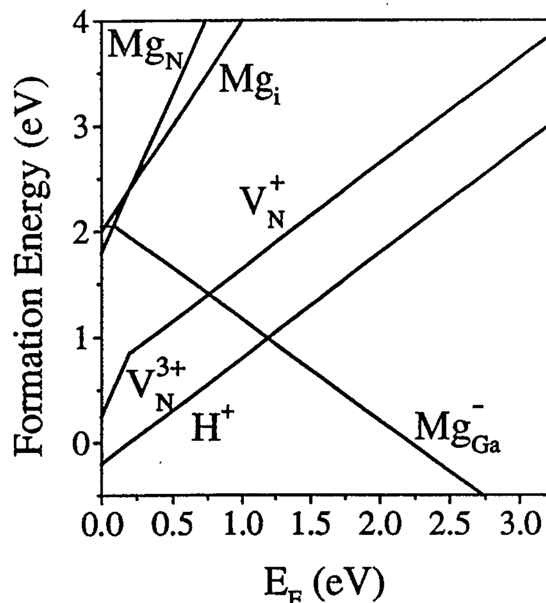

FIGURE 2 Formation energy as a function of Fermi energy for Mg in different configurations (Ga-substitutional, N-substitutional and interstitial configuration). Also included are the native defects (nitrogen vacancies) and interstitial H.

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.

REFERENCES

[1] J. Neugebauer, C.G. Van de Walle [*Phys. Rev. B (USA)* vol.50 (1994) p.8067]
[2] J. Neugebauer, C.G. Van de Walle [*Festköerperprobleme (Germany)* vol.35 (1996) p.25]
[3] R. Stumpf, M. Scheffler [*Comput. Phys. Commun. (Netherlands)* vol.79 (1994) p.447]
[4] J. Neugebauer, C.G. Van de Walle [*Mater. Res. Soc. Symp. Proc. (USA)* vol.408 (1996) p.43]
[5] J. Neugebauer, C.G. Van de Walle [*Proc. ICPS-22* (World Scientific, Singapore, 1995) p.2327]
[6] W. Seifert, R. Franzheld, E. Butter, H. Sobotta, V. Riede [*Cryst. Res. Technol. (Germany)* vol.18 (1983) p.383]
[7] B.-C. Chung, M. Gershenzon [*J. Appl. Phys. (USA)* vol.72 (1992) p.651]
[8] W. Götz, N.M. Johnson, C. Chen, H. Liu, C. Kuo, W. Imler [*Appl. Phys. Lett. (USA)* vol.68 (1996) p.3114]
[9] W. Götz, J. Walker, L.T. Romano, N.M. Johnson [*Mater. Res. Soc. Symp. Proc. (USA)* vol.449 (1997) p.525]
[10] P. Perlin et al [*Mater. Res. Soc. Symp. Proc. (USA)* vol.449 (1997) p.519]
[11] C. Wetzel et al [*Phys. Rev. Lett. (USA)* vol.78 (1997) p.3923]
[12] C.G. Van de Walle [*Phys. Rev. B (USA)* vol.57 (1998) p.2033]

[13] P. Mooney [in *Deep Centers in Semiconductors* Ed. S.T. Pantelides (Gordon and Breach, Yverdon, Switzerland, 1992) p.643]
[14] C.H. Park, D.J. Chadi [*Phys. Rev. B (USA)* vol.55 (1997) p.12995]
[15] H.G. Lee, M. Gershenzon, B.L. Goldenberg [*J. Electron. Mater. (USA)* vol.20 (1991) p.621]
[16] M.D. McCluskey, N.M. Johnson, C.G. Van de Walle, D.P. Bour, M. Kneissl, W. Walukiewicz [*Phys. Rev. Lett. (USA)* vol.80 (1998) p.4008]
[17] G.-C. Yi, B.W. Wessels [*Appl. Phys. Lett. (USA)* vol.69 (1996) p.3028]
[18] D.P. Bour et al [*Mater. Res. Soc. Symp. Proc. (USA)* vol.449 (1997) p.509]
[19] J. Neugebauer, C.G. Van de Walle [*Mater. Res. Soc. Symp. Proc. (USA)* vol.395 (1996) p.645]
[20] C. Johnson, J.Y. Lin, H.X. Jiang, M.A. Khan, C.J. Sun [*Appl. Phys. Lett. (USA)* vol.68 (1996) p.1808]; J.Z. Li, J.Y. Lin, H.X. Jiang, A. Salvador, A. Botchkarev, H. Morkoc [*Appl. Phys. Lett. (USA)* vol.69 (1996) p.1474]
[21] C.G. Van de Walle [*Phys. Rev. B (USA)* vol.56 (1997) p.R10020]
[22] M.D. Bremser et al [*MRS Internet J. Nitride Semicond. Res. (USA)* vol.1 (1996) p.8]
[23] C. Stampfl, C.G. Van de Walle [*Appl. Phys. Lett. (USA)* vol.72 (1998) p.459]
[24] J. Neugebauer, C.G. Van de Walle [*Proc. ICPS-23* (World Scientific, Singapore, 1996) p.2849]
[25] F. Bernardini, V. Fiorentini, A. Bosin [*Appl. Phys. Lett. (USA)* vol.70 (1997) p.2990]
[26] O. Brandt, H. Yang, H. Kostial, K.H. Ploog [*Appl. Phys. Lett. (USA)* vol.69 (1996) p.2707]

A8.2 Native point defects in GaN and related compounds

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A INTRODUCTION

Native defects can have a profound effect on the electronic properties of semiconductors. They often act as sources of compensation; for instance, when acceptors are introduced into the material, a native defect that acts as a donor may form spontaneously, thereby counteracting the intended doping. Native defects have often been blamed for doping problems; however, they are only one of the potential reasons why doping efficiencies may be lower than expected. Other causes for doping problems include limited solubility of the dopant, high ionisation energy of the dopant or incorporation of the dopant impurity in other configurations in the lattice. Some of these causes are discussed in Datareview A8.1.

Native defects have sometimes been invoked not just as sources of compensation, but as sources of doping. The nitrogen vacancy in GaN is a prime example: for a long time the nitrogen vacancy was thought to be the source of n-type conductivity in GaN. As early as 1983 it was pointed out that unintentional incorporation of oxygen was a more likely explanation [1]. Still, it is only recently that unintentional impurities have become widely accepted as the source of n-type conductivity, thanks in part to contributions from first-principles theory (see Datareview A8.1). In this Datareview we will describe some of those theoretical results, for vacancies as well as other native defects (self-interstitials and antisites). Experimental information about native defects in the nitrides is very scarce at this time; we will include references where available.

B NATIVE DEFECTS IN GaN

Formation energies for all native point defects in GaN, in all relevant charge states, are shown in FIGURE 1. These results were obtained from first-principles calculations [2-4]. Similar results for native defects were obtained by Boguslawski et al [5]. These references also contain detailed information about the atomic structure of each of the defects. A definition of formation energies and a description of the computational approach can be found in Datareview A8.1. For each charge state of each defect we show only the line segment that gives rise to the overall lowest energy. Thus, the change in slope of the lines represents a change in the charge state of the defect.

FIGURE 1 shows that self-interstitial and antisite defects are high-energy defects in GaN, and are thus unlikely to occur during growth. These defects can still be created by electron irradiation or ion implantation, of course. One such defect, created by electron irradiation, has been identified as a complex involving interstitial Ga [6].

Nitrogen vacancies (V_N) do behave as donors (notice the dependence on Fermi energy; an increase of formation energy with E_F is indicative of donors). When purposely created, for instance during irradiation or ion implantation, nitrogen vacancies will increase the electron concentration [7]. However, their high formation energy makes it very unlikely that nitrogen vacancies would form spontaneously during growth of undoped or n-type GaN, and hence they cannot be responsible for n-type conductivity. As discussed in Datareview A8.1, unintended n-type conductivity in GaN must therefore be attributed to incorporation of donor impurities such as Si or O. Note, however, that nitrogen vacancies have a low formation energy in p-type GaN, making them a likely compensating centre for acceptor doping, as discussed in Datareview A8.1.

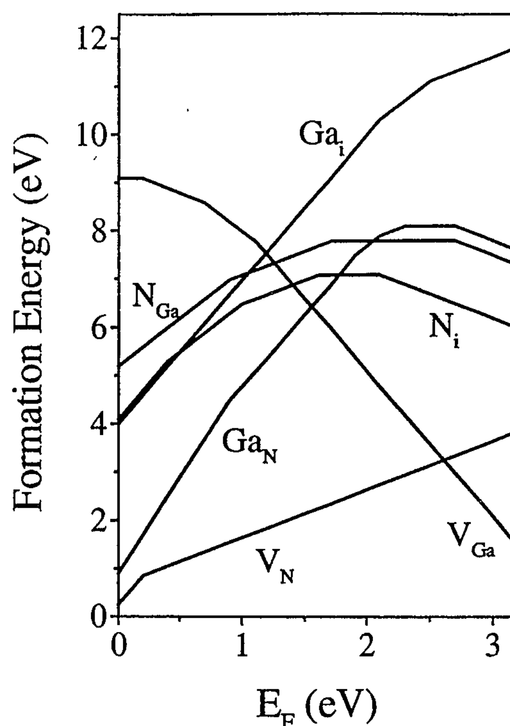

FIGURE 1 Formation energy as a function of Fermi level for native point defects in GaN under Ga-rich conditions. $E_F = 0$ corresponds to the top of the valence band.

In n-type GaN the lowest-energy native defect is the gallium vacancy (V_{Ga}), a triple acceptor. This defect plays a role in donor compensation (see Datareview A8.1), as well as in the frequently observed yellow luminescence (see Datareview A8.7).

C NATIVE DEFECTS IN AlN

First-principles calculations have also been performed for formation energies of native defects in AlN [8,9]. The main conclusions are similar to those for GaN: self-interstitials and antisites are high in energy - with the exception of the Al interstitial in cubic AlN, which is a triple donor and could act as a compensating centre in p-type material.

The nitrogen vacancy is a high-energy defect in n-AlN, but has a relatively low energy in p-AlN. V_N behaves as a donor which can potentially donate one, two or three electrons; however, only the V^+_N and V^{3+}_N charge states are stable. The formation energy of V_N is lower in AlN than in GaN, and therefore compensation of p-type $Al_xGa_{1-x}N$ by nitrogen vacancies becomes increasingly severe for increasing x (see Datareview A8.1).

The behaviour of V_{Al} is similar to that of V_{Ga} in GaN, but because of the larger bandgap of AlN the formation energy of V^{3-}_{Al} becomes significantly lower than that of V^{3-}_{Ga} for Fermi-level positions high in the gap. This defect will therefore increasingly compensate the n-type conductivity in $Al_xGa_{1-x}N$ with increasing x, as discussed in Datareview A8.1.

D CONCLUSION

Detailed theoretical information is available about native defects in GaN and AlN, leading to specific predictions about electronic behaviour and compensation of donors or acceptors. These predictions are

in good agreement with experimental observations of doping efficiencies, as discussed in Datareview A8.1. However, direct experimental observations of the atomic and electronic structure of native defects are still lacking.

REFERENCES

[1] W. Seifert, R. Franzheld, E. Butter, H. Sobotta, V. Riede [*Cryst. Res. Technol. (Germany)* vol.18 (1983) p.383]

[2] J. Neugebauer, C.G. Van de Walle [*Phys. Rev. B (USA)* vol.50 (1994) p.8067]

[3] J. Neugebauer, C.G. Van de Walle [*Festköerperprobleme (Germany)* vol.35 (1996) p.25]

[4] J. Neugebauer, C.G. Van de Walle [*Appl. Phys. Lett. (USA)* vol.69 (1996) p.503]

[5] P. Boguslawski, E.L. Briggs, J. Bernholc [*Phys. Rev. B (USA)* vol.51 (1995) p.255]

[6] M. Linde, S.J. Uftring, G.D. Watkins, V. Härle, F. Scholz [*Phys. Rev. B (USA)* vol.55 (1997) p.R10177]

[7] D.C. Look, D.C. Reynolds, J.W. Hemsky, J.R. Sizelove, R.L. Jones, R.J. Molnar [*Phys. Rev. Lett. (USA)* vol.79 (1997) p.2273]

[8] T. Mattila, R.M. Nieminen [*Phys. Rev. B (USA)* vol.54 (1996) p.16676]; T. Mattila, R.M. Nieminen [*Phys. Rev. B (USA)* vol.55 (1997) p.9571]

[9] C. Stampfl, C.G. Van de Walle [*Appl. Phys. Lett. (USA)* vol.72 (1998) p.459]

A8.7 Yellow luminescence in GaN

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A INTRODUCTION

The yellow luminescence (YL) in GaN is a broad luminescence band centred around 2.2 eV. The YL appears to be a universal feature: it has been observed in bulk GaN crystallites as well as in epitaxial layers grown by different techniques. The intensity can vary over a wide range, with good samples exhibiting almost no YL.

The origins of the YL have been widely debated. Ogino and Aoki [1] proposed a model in which the YL is a transition between a shallow donor and a deep acceptor level. We will see that a variety of experiments now confirm this model. Proposals for the microscopic nature of the deep level have included a complex between a Ga vacancy (V_{Ga}) and a carbon atom [1], an N_{Ga} antisite [2] and an isolated V_{Ga} [3,4] (or a complex between V_{Ga} and oxygen [4]).

At this time the gallium vacancy (in isolated form or complexed with an impurity) appears to be the most likely source of the yellow luminescence. In this Datareview we will summarise the available evidence.

B FIRST-PRINCIPLES CALCULATIONS

B1 Gallium Vacancies

First-principles results for V_{Ga} are presented in Datareview A8.2. The gallium vacancy is an acceptor-type defect, and hence its formation energy decreases with increasing Fermi level. Gallium vacancies are therefore more likely to occur in n-type than in p-type GaN. The Ga vacancy has a deep level (the 2-/3- transition level) about 1.1 eV above the valence band [4], as illustrated in FIGURE 1. Transitions between the conduction band (or shallow donors) and this deep level therefore exhibit the correct energy to explain the YL.

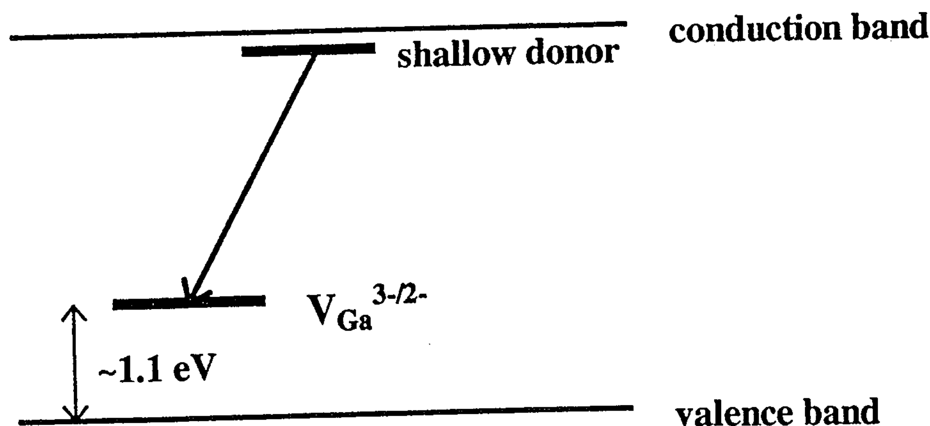

FIGURE 1 Schematic illustration of levels involved in the yellow luminescence in GaN. Gallium vacancies introduce a deep acceptor level about 1.1 eV above the valence band. Transitions between shallow donors and the deep acceptor level give rise to the YL.

B2 Complexing with Donor Impurities

Gallium vacancies can form complexes with donor impurities in GaN [4]. The V_{Ga}-Si_{Ga} complex has a rather small binding energy, due to its components being only second-nearest neighbours. The V_{Ga}-O_N complex, on the other hand, has a large binding energy (1.8 eV), and can therefore play a role in enhancing the concentration of Ga vacancies. The electronic structure of this complex is very similar to that of the isolated gallium vacancy, giving rise to a deep level again about 1.1 eV above the valence band. The presence of oxygen can therefore enhance the concentration of Ga vacancies and hence the YL. The formation of complexes involving Ga vacancies probably causes a shift in the transition energy, contributing to a broadening of the luminescence line. Other factors contributing to the width of the line could be strain and proximity to extended defects.

C EXPERIMENTAL EVIDENCE

C1 Observation of Ga Vacancies by Positron Annihilation

The most direct evidence of a correlation between Ga vacancies and YL is based on positron annihilation measurements [5]. These experiments provide a direct probe of vacancies in the sample. It was found that the concentration of V_{Ga} correlates with the intensity of the YL, providing direct evidence for the involvement of the V_{Ga} acceptor levels in the YL.

C2 n-Type versus p-Type GaN

Gallium vacancies are more likely to form in n-type than in p-type GaN. This trend is consistent with experimental observations indicating suppression of the YL in p-type material [6-8]. Conversely, an increase in n-type doping increases the intensity of the YL [9-11].

C3 Ga-Rich versus N-Rich

It is obvious that the concentration of gallium vacancies will be lower in Ga-rich material. The YL was indeed found to be suppressed in samples grown by metal-organic chemical vapour deposition (MOCVD) with higher trimethyl-gallium (TMGa) flow rates [3,6]. The YL was also found to be stronger in samples grown at higher microwave power in electron-cyclotron resonance (ECR) assisted molecular beam epitaxy (MBE); this could be consistent with higher V_{Ga} concentrations when the growth is more N-rich, provided no plasma-induced damage is involved [12]. Finally, it has been observed that the YL is weak in material grown by hydride vapour phase epitaxy (HVPE) [13], which could be consistent with growth conditions in HVPE being more Ga-rich than in MOCVD.

It should be noted that the formation energy of a V_{Ga}-O_N complex does not depend on the atomic chemical potentials. In oxygen-containing samples one therefore does not necessarily expect the YL to be reduced under Ga-rich conditions.

C4 Recombination Mechanism

Various experiments have linked the YL with a deep level located about 1 eV above the valence band [2,14,15]. This is in agreement with the calculated position of the defect level induced by the Ga vacancy [4] (see FIGURE 1). In addition, the calculated pressure dependence of this level is also consistent with experiment [2].

C5 Role of Oxygen

First-principles calculations indicate that Ga vacancies are more likely to form in the presence of oxygen. This is a likely explanation for the increase in YL intensity in the neighbourhood of the

interface with the sapphire substrate [16], where the oxygen concentration is also known to be higher [17,18].

C6 Role of Carbon

It has been suggested that the YL is related to the presence of carbon in the material [1,19]. Extensive first-principles investigations of carbon on different sites and as a component of various complexes did not produce any defect with properties consistent with the known facts about the YL [4]. The presence of carbon in material that exhibits YL therefore appears to be merely coincidental; indeed, an increase in n-type doping facilitates the incorporation of C (an acceptor) at the same time as enhancing the YL.

C7 Ion Implantation

Implantation with a variety of elements produced a broad luminescence band around 2.15 eV [20]. Implantation damage is likely to result in preferential creation of Ga-site defects; indeed, the displacement energy threshold in III-V compounds tends to be lower for the cation site [21]. Formation of Ga vacancies is thus likely during implantation, consistent with the increase in the YL.

D SIMILARITY WITH SA CENTRES IN II-VI COMPOUNDS

It is useful to point out the similarity between the YL in GaN and the so-called self-activated (SA) luminescence in II-VI compounds. Metal vacancies and their complexes with donor impurities are well known in II-VI compounds (e.g. ZnS, ZnSe). The metal vacancy complexes (the so-called SA centres) exhibit features which are strikingly similar to the YL: recombination between a shallow donor-like state and a deep acceptor state, and a broad luminescence band of Gaussian shape [22,23].

E CONCLUSION

Strong theoretical as well as experimental evidence is now available identifying gallium vacancies as the source of the yellow luminescence in GaN.

REFERENCES

[1] T. Ogino, M. Aoki [*Jpn. J. Appl. Phys. (Japan)* vol.19 (1980) p.2395]

[2] T. Suski et al [*Appl. Phys. Lett. (USA)* vol.67 (1995) p.2188]

[3] X. Zhang, P. Kung, A. Saxler, D. Walker, T. Wang, M. Razeghi [*Acta Phys. Pol. A (Poland)* vol.88 (1995) p.601]

[4] J. Neugebauer, C.G. Van de Walle [*Appl. Phys. Lett. (USA)* vol.69 (1996) p.503]

[5] K. Saarinen et al [*Phys. Rev. Lett. (USA)* vol.79 (1997) p.3030]

[6] X. Zhang, P. Kung, D. Walker, A. Saxler, M. Razeghi [*Mater. Res. Soc. Symp. Proc. (USA)* vol.395 (1996) p.625]

[7] W. Götz, N. Johnson, J. Walker, D.P. Bour, H. Amano, I. Akasaki [*Inst. Phys. Conf. Ser. (UK)* no.142 (1996) p.1031]

[8] W. Kim, A. Salvador, A.E. Botchkarev, O. Aktas, S.N. Mohammad, H. Morkoç [*Appl. Phys. Lett. (USA)* vol.69 (1996) p.559]

[9] N. Kaneda, T. Detchprohm, K. Hiramatsu, N. Sawaki [*Jpn. J. Appl. Phys. (Japan)* vol.35 (1996) p.L468]

[10] E.F. Schubert, I.D. Goepfert, J.M. Redwing [*Appl. Phys. Lett. (USA)* vol.71 (1997) p.3224]

[11] I.-H. Lee, I.-H. Choi, C.R. Lee, S.K. Noh [*Appl. Phys. Lett. (USA)* vol.71 (1997) p.1359]

[12] R. Singh, R.J. Molnar, M.S. Ünlü, T.D. Moustakas [*Appl. Phys. Lett. (USA)* vol.64 (1994) p.336]

[13] W. Götz, L.T. Romano, B.S. Krusor, N.M. Johnson, R.J. Molnar [*Appl. Phys. Lett. (USA)* vol.69 (1996) p.242]

[14] F.J. Sánchez et al [*MRS Internet J. Nitride Semicond. Res. (USA)* vol.1 (1996) article 7]

[15] E. Calleja et al [*Phys. Rev. B (USA)* vol.55 (1997) p.4689]

[16] D.M. Hofmann et al [*Phys. Rev. B (USA)* vol.52 (1995) p.16702]

[17] W. Götz, J. Walker, L.T. Romano, N.M. Johnson [*Mater. Res. Soc. Symp. Proc. (USA)* vol.449 (1997) p.525]

[18] G. Popovici, W. Kim, A. Botchkarev, H. Tang, H. Morkoç, J. Solomon [*Appl. Phys. Lett. (USA)* vol.71 (1997) p.3385]

[19] R. Niebuhr, K. Bachem, K. Dombrowski, M. Maier, W. Pletschen, U. Kaufmann [*J. Electron. Mater. (USA)* vol.24 (1995) p.1531]

[20] J.I. Pankove, J.A. Hutchby [*J. Appl. Phys. (USA)* vol.47 (1976) p.5387]

[21] K.W. Böer [*Survey of Semiconductor Physics* (Van Nostrand Reinhold, New York, 1990) p.629]

[22] R.K. Watts (Ed.) [*Point Defects in Crystals* (John Wiley & Sons, New York, 1977) p.248ff]

[23] P.J. Dean [*Phys. Status Solidi A (Germany)* vol.81 (1984) p.625]

A8.8 Hydrogen and acceptor compensation in GaN

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A INTRODUCTION

Hydrogen has strong effects on the properties of GaN. Many growth techniques, such as metal-organic chemical vapour deposition (MOCVD) or hydride vapour phase epitaxy (HVPE), expose the growing material to large concentrations of hydrogen. The presence of hydrogen has particularly important consequences for p-type doping of the material: hydrogen incorporated during growth leads to passivation of acceptors, and a post-growth processing step is required to render the acceptors electrically active. The presence of hydrogen during growth is actually quite beneficial: it suppresses compensation, and enhances the solubility of acceptors.

B ISOLATED INTERSTITIAL HYDROGEN

B1 Theory

The behaviour of hydrogen in GaN has been analysed in detail based on first-principles calculations [1-3]. FIGURE 1 shows the calculated formation energy of hydrogen in various charge states as a function of Fermi level. The formation energy is defined as the energy difference between hydrogen at an interstitial position in GaN, and hydrogen in a reservoir (in this case free H_2 molecules) [1]; for a formal definition of formation energies, see Datareview A8.1, EQN (1). One immediate conclusion from FIGURE 1 is that the formation energy of hydrogen is lower in p-type GaN than in n-type GaN, corresponding to a much higher solubility in p-type than in n-type GaN.

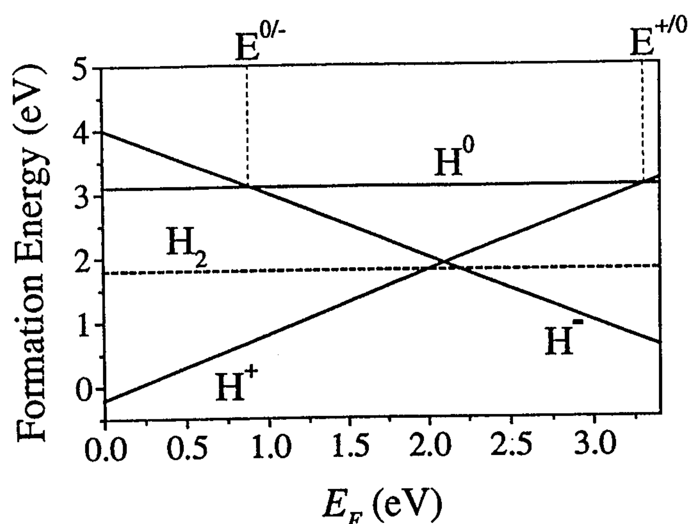

FIGURE 1 Formation energies as a function of Fermi level for H^+, H^0 and H^- (solid lines), and for an H_2 molecule (dashed line) in GaN [1]. $E_F = 0$ corresponds to the top of the valence band. The formation energy is referenced to the free H_2 molecules.

In p-type GaN, H behaves as a donor (H^+); it thus compensates acceptors. The preferred location for H^+ is at the antibonding site behind a nitrogen atom. The diffusion barrier for H^+ is only 0.7 eV, which indicates a high diffusivity at moderate to high temperatures. In n-type GaN, H behaves as an acceptor (H^-); its most stable site is at the antibonding site behind a Ga atom. The migration barrier for H^- is

3.4 eV, indicating a very low diffusivity. For Fermi-level positions below ≈2.1 eV H^+ is favoured; higher Fermi-level positions favour H^-. The neutral charge state is never stable [1]. This is characteristic of a so-called negative-U centre.

FIGURE 1 also shows the formation energy of H_2 molecules in GaN. It is clear that H_2 is unstable with respect to dissociation into monatomic hydrogen.

B2 Experiment

Hydrogen is easily incorporated into GaN during many different process steps, including boiling in water, wet chemical etching, dielectric deposition using SiH_4 or dry etching [4,5]. The ability to diffuse hydrogen into GaN at moderate temperatures depends strongly on the electrical conductivity type. Samples of n-type versus p-type GaN were exposed to monatomic deuterium at specified temperatures for one hour in a remote microwave plasma [6]; depth profiles of deuterium were obtained with SIMS. The experimental results indicate that hydrogen readily diffuses and incorporates in p-type GaN at temperatures ≥600°C but not in n-type GaN. These results are in full agreement with the first-principles calculations discussed above.

C STRUCTURE OF ACCEPTOR-HYDROGEN COMPLEXES

C1 Theory

The behaviour of isolated interstitial hydrogen, as discussed in Section B, provides crucial information about interaction with impurities. Since both the solubility and the diffusivity of hydrogen in n-type GaN are low, hydrogen-donor complexes will rarely form,
and we focus on complexes with acceptors.

In p-type GaN hydrogen occurs in the positive charge state and is located in an antibonding site behind a nitrogen atom; it is electrostatically attracted to negatively charged acceptors, and also assumes the antibonding configuration. In the case of Mg acceptors, this means that H is not located next to the Mg atom, but rather binds to an N atom which is a neighbour of the acceptor (see FIGURE 2) [1,2]. This is an unusual structure for an acceptor-hydrogen complex; in other semiconductors hydrogen assumes the bond-centre position when binding to acceptors [7]. As a direct consequence the vibrational frequency of the complex is not representative of a Ga-H bond, but rather of an N-H bond. The calculated vibrational frequency (in the harmonic approximation) is 3360 cm^{-1}. Anharmonic effects may lower this frequency by as much as 170 cm^{-1} [8].

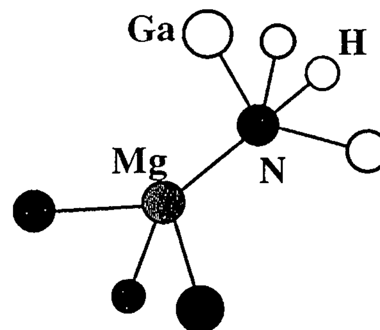

FIGURE 2 Schematic illustration of the structure of an Mg-H complex in GaN. Hydrogen resides in an antibonding position behind a nitrogen atom.

C2 Experiment

Determination of the local vibrational modes (LVM) of the Mg-H complex in GaN provides satisfying confirmation of the significance of hydrogen in GaN and useful information, when compared with theory, on the structure of the complex. At the present time the stretch frequency is in fact the only reliably established physical parameter available from experiment for the Mg-H complex in GaN.

Fourier-transform infrared absorption spectroscopy was performed on Mg-doped GaN grown by MOCVD [9]. The as-grown sample was semi-insulating and displayed an LVM at 3125 cm^{-1}. After

thermal activation the sample became p-type conductive and the intensity of the LVM was reduced. Subsequent exposure to monatomic deuterium at 600°C for two hours increased the resistivity and caused a new absorption line to appear at 2321 cm^{-1}. This line disappeared after a thermal activation treatment. The isotopic shift clearly established the presence of hydrogen in the complex. The assignment of the LVM to the stretch mode of the Mg-H complex is in good agreement with the calculated H-stretch frequency which establishes that the Mg-H complex contains a strong N-H bond.

D ROLE OF HYDROGEN IN p-TYPE DOPING OF GaN

D1 Theory

First-principles calculations show that hydrogen binds to Mg acceptors with a binding energy of 0.7 eV [1]. This value implies that at the growth temperature hydrogen is not bound to the acceptors; during cooldown the hydrogen atoms diffuse rapidly and eventually form hydrogen-acceptor complexes.

FIGURE 3 compares the formation energy of hydrogen in p-GaN with that of the nitrogen vacancy. Formation energies of native defects and dopant impurities are discussed in Datareviews A8.1 and A8.2. In the absence of hydrogen, nitrogen vacancies are the dominant compensating centres, and due to charge neutrality the Fermi level will be located near the point where the formation energies of V^{+}_{N} and Mg^{-}_{Ga} are equal. When hydrogen is present, however, compensation by nitrogen vacancies is suppressed. The Mg concentration is also increased, compared to the hydrogen-free case. This can be understood by inspection of the formation energies in FIGURE 3: since the formation energy of hydrogen is lower than that of V^{+}_{N}, the Fermi level equilibrium point is moved higher in the gap, leading to a lower formation energy and hence higher concentration of Mg. Incorporation of hydrogen is therefore beneficial in two respects: suppression of native defects, and enhancement of the acceptor concentration.

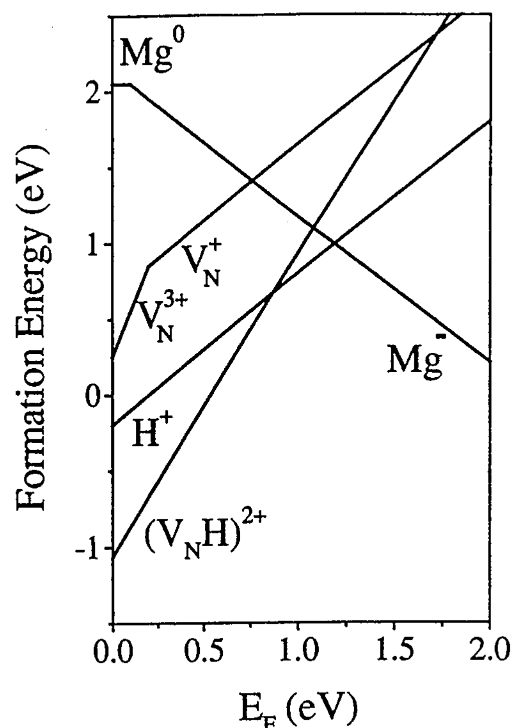

FIGURE 3 Formation energy as a function of Fermi level for Mg, nitrogen vacancies, interstitial H and hydrogen-vacancy complexes in GaN [1,14].

Incorporation of hydrogen of course has the downside that complex compensation of the acceptors occurs. The dissociation barrier of the Mg-H complex was estimated to be 1.5 eV [1]. This value should allow dissociation of the complex at temperatures of a few hundred °C. Experimentally, however, temperatures exceeding 600°C have been found necessary to activate Mg-doped MOCVD-grown GaN [10,11]. This indicates that the activation process does not merely consist of dissociating Mg-H complexes. When hydrogen leaves the Mg acceptor, it still behaves as a donor, and therefore can still compensate the acceptor as long as its remains in the p-type layer. The hydrogen therefore has to be removed from the p-type layer (e.g. into the substrate or through the surface); alternatively, the hydrogen can be neutralised, e.g. by binding to extended defects. Formation of H_2 molecules, which is common after acceptor passivation in other semiconductors, is not possible in GaN because of the high formation energy of H_2 (see Section B1).

D2 Experiment

The important role played by hydrogen in p-type GaN was established when it was shown that MOCVD-grown Mg-doped films, which are highly resistive after growth, become p-type conductive after thermal annealing in an N_2 ambient [10]. Annealing the samples in an NH_3 ambient led to a significant increase in the resistivity. It was suggested that atomic hydrogen produced by NH_3 dissociation was responsible for the passivation of acceptors, hydrogen passivation of acceptors already being a well-established phenomenon in elemental and other compound semiconductors [12].

The theoretical framework for hydrogen interactions with acceptors presented in Section D1 explains the necessity of an activation procedure when Mg-doped GaN is grown by MOCVD. During cooldown acceptor-hydrogen complexes are formed. In order to activate the Mg, the complexes have to be dissociated and hydrogen neutralised or removed from the p-type layer. This can be accomplished by treatments such as low-energy electron-beam irradiation (LEEBI) [13] or thermal annealing [10].

The mechanism by which LEEBI treatment [13] activates acceptors is still poorly understood. The irradiation process can generate electron-hole pairs; these pairs could either directly provide the energy for releasing hydrogen from the acceptor, or the presence of minority carriers could lower the dissociation barrier. Alternatively, the irradiation process may cause local heating that effectively leads to thermal dissociation.

Detailed studies of the activation kinetics of Mg acceptors during thermal annealing were reported in [11]. Mg-doped samples grown by MOCVD were annealed incrementally for five minutes at temperatures ranging from 500°C to 850°C. The resistivity decreased significantly after the 600°C annealing step and reached a value of about 3 Ω cm at 300 K after annealing at 850°C. Samples annealed above 700°C exhibited hole conduction in an acceptor impurity band for measurement temperatures below 200 K. These results are consistent with the picture of Mg-H complexes being present in as-grown, Mg-doped GaN; only a fraction of Mg atoms act as acceptors and the material is semi-insulating. The absence of impurity-band conduction after the 600°C anneal, and its appearance after the 700°C anneal, clearly indicate that the activation of Mg acceptors is due to the generation of Mg-related acceptor states in the bandgap of GaN, and therefore strongly supports the existence of Mg-H complexes in the as-grown material.

E INTERACTIONS OF HYDROGEN WITH NATIVE DEFECTS

The interactions of hydrogen with native point defects in GaN were studied with first-principles calculations [14]. Since antisites and self-interstitials are very unlikely to form in GaN (see Datareview A8.2) the investigations focused on H interacting with vacancies. This interaction is often described in terms of tying off of dangling bonds. This picture does not apply in the case of the nitrogen vacancy, which is surrounded by Ga atoms at a distance of 1.95 Å from the centre of the vacancy; a typical Ga-H bond distance is too large for more than one H to fit inside the vacancy. The calculated binding energy of the $(V_NH)^{2+}$ complex, expressed with respect to interstitial H in the positive charge state, is 1.56 eV; the formation energy of this complex is included in FIGURE 3. This complex has been proposed [14] to be involved in the appearance and disappearance of photoluminescence (PL) lines during post-growth annealing of Mg-doped layers grown by MOCVD [11]. The as-grown material contains a certain concentration of hydrogenated nitrogen vacancies. Annealing causes these complexes to dissociate; the calculated removal energy is consistent with complex dissociation around 500°C. The resulting nitrogen vacancies have a level near the valence band, which may be responsible for the PL line around 2.9 eV (~420 nm) (see Datareview A8.2).

In the case of the gallium vacancy (V_{Ga}) one, two, three or four H atoms can be accommodated in the vacancy, and levels are removed from the bandgap as more hydrogens are attached. Distinct N-H bonds are formed with a bond length of about 1.02 Å and vibrational modes between 3100 cm^{-1} and

3500 cm^{-1}. Hydrogenated gallium vacancies with one or two H atoms behave in much the same way as the unhydrogenated kind; they may therefore contribute to compensation of donors as well as to the yellow luminescence (see Datareviews A8.1, A8.2 and A8.7).

F CONCLUSION

Hydrogen plays an important role in p-type GaN. Hydrogen incorporated during growth (in MOCVD and HVPE) passivates acceptors; a post-growth treatment is required to activate the acceptors. However, the presence of hydrogen during growth is quite beneficial, since it efficiently suppresses compensation by nitrogen vacancies and significantly enhances the Mg concentration. Most of the detailed knowledge about hydrogen interactions with nitrides right now is based on computational studies. Experimental work has established the main qualitative features, but additional work will be needed to obtain quantitative assessments.

REFERENCES

[1] J. Neugebauer, C.G. Van de Walle [*Phys. Rev. Lett. (USA)* vol.75 (1995) p.4452]

[2] J. Neugebauer, C.G. Van de Walle [*Appl. Phys. Lett. (USA)* vol.68 (1996) p.1829]

[3] A. Bosin, V. Fiorentini, D. Vanderbilt [*Mater. Res. Soc. Symp. Proc. (USA)* vol.395 (1996) p.503]

[4] S.J. Pearton, J.W. Lee, C. Yuan [*Appl. Phys. Lett. (USA)* vol.68 (1996) p.2690]

[5] S.J. Pearton et al [*Appl. Phys. Lett. (USA)* vol.69 (1996) p.1879]

[6] W. Götz, N.M. Johnson, J. Walker, D.P. Bour, H. Amano, I. Akasaki [*Appl. Phys. Lett. (USA)* vol.67 (1995) p.2666]

[7] C.G. Van de Walle [*Physica B (Netherlands)* vol.170 (1991) p.21]

[8] B.G. Johnson, P.M.W. Gill, J.A. Pople [*J. Chem. Phys. (USA)* vol.98 (1993) p.5612]

[9] W. Götz, N.M. Johnson, D.P. Bour, M.D. McCluskey, E.E. Haller [*Appl. Phys. Lett. (USA)* vol.69 (1996) p.3725]

[10] S. Nakamura, N. Iwasa, M. Senoh, T. Mukai [*Jpn. J. Appl. Phys. (Japan)* vol.31 (1992) p.1258]

[11] W. Götz, N.M. Johnson, J. Walker, D.P. Bour, R.A. Street [*Appl. Phys. Lett. (USA)* vol.68 (1996) p.667]

[12] J.I. Pankove, N.M. Johnson (Eds.) [*Semicond. Semimet. (USA)* vol.34 (1991)]

[13] H. Amano, M. Kito, K. Hiramatsu, I. Akasaki [*Jpn. J. Appl. Phys. (Japan)* vol.28 (1989) p.L2112]

[14] C.G. Van de Walle [*Phys. Rev. B (USA)* vol.56 (1997) p.R10020]