Invited Paper

Defects, doping and interfaces in III-V nitrides

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ABSTRACT

We describe the use of first-principles calculations to address problems related to defects, doping, and band-structure engineering in III-V nitrides. For n-type doping it is found that nitrogen vacancies are too high in energy to be formed during growth, but silicon and oxygen readily incorporate as donors. The properties of oxygen, including DX-center formation, support it as the main cause of unintentional n-type conductivity. For p-type doping we find that the solubility of Mg is the main factor limiting the hole concentration in GaN. We discuss the beneficial effects of hydrogen during acceptor doping. Compensation of acceptors by nitrogen vacancies may occur, becoming increasingly severe as x increases in $Al_xGa_{1-x}N$ alloys. Acceptors other than Mg are also investigated. Finally, we discuss our first-principles investigations of the atomic and electronic structure of heterojunction interfaces between the III-nitrides, and provide values for band lineups.

Keywords: GaN, nitrides, first-principles calculations, vacancies, hydrogen, magnesium, oxygen, interfaces, band offsets

1. INTRODUCTION

We have recently witnessed fast and impressive progress in materials preparation and device fabrication of III-V nitride semiconductors.[1] A number of problems still exist, however, which have to be addressed in order to exploit the full potential of this materials system.

Control of doping is crucial for device fabrication; wide-band-gap semiconductors such as GaN have long suffered from lack of control of the doping levels. For n-type doping, the outstanding problems include (i) suppression of background n-type conductivity; (ii) compensation at high doping levels; and (iii) n-type doping of AlGaN alloys. For p-type doping, the main issue concerns increasing the achievable hole concentrations; this requires an understanding of (i) the factors limiting doping efficiency, such as high ionization energies, solubility, and compensation by native defects; (ii) potential metastabilities (as evidenced in persistent photoconductivity); (iii) the role of hydrogen; and (iv) the reasons for increased doping difficulties in AlGaN alloys.

In this paper we discuss how a theoretical approach for native defects and dopant impurities, combined with state-of-the-art first-principles calculations, can be used to understand the various factors that govern doping. Section 2 contains a brief description of the theoretical apporach. In Section 3 we discuss our results for native defects in GaN. An important conclusion is that nitrogen vacancies are not responsible for the commonly observed unintentional n-type conductivity. In Section 4 we will show that the unintentional n-type doping is usually due to oxygen. We discuss the behavior of oxygen in AlGaN alloys, where a DX transition is predicted to occur. Silicon donors do not exhibit this transition, and it is also absent in the zinc-blende phase. We will also discuss gallium vacancies, which act as compensating centers in n-type GaN, and which are the most likely source of the "yellow luminescence."

Section 5 contains a discussion of p-type doping, which is now routinely performed in GaN with Mg acceptors and using a post-growth activation step in material grown by MOCVD (metal-organic chemical vapor deposition). Hydrogen plays a crucial role in this process. However, p-type doping levels are still lower than desirable for low-resistance cladding layers and ohmic contacts. We will show that Mg solubility is the determining factor limiting the hole concentration in GaN; incorporation of Mg on interstitial sites or on substitutional nitrogen sites is found to be unfavorable. We will also discuss the prospects of other acceptor impurities for achieving higher doping levels. Some degree of compensation by nitrogen vacancies occurs, and we will discuss the effect of increasing x in $Al_xGa_{1-x}N$ alloys on the doping efficiency.

Section 6 describes theoretical results for nitride interfaces and band offsets. The valence-band offset between InGaN and GaN will be shown to be smaller than expected. Effects of strain on band offsets will also be discussed.

Section 7 summarizes and concludes the paper.

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2. THEORETICAL APPROACH

Key parameters in our approach are obtained from first-principles calculations that do not require any adjustable parameters or any input from experiment. The computations are based on density-functional theory,[2] using a supercell geometry and soft Troullier-Martins pseudopotentials.[3] The effect of *d* electrons in GaN is taken into account either through the so-called non-linear core correction[4] or by explicit inclusion of the *d* electrons as valence electrons; the latter proved to be necessary for obtaining accurate results in certain cases.[5] Further details of the computational approach can be found in Refs. 6, 7, and 8.

A key quantity describing the behavior of defects and impurities is their *formation energy*, E^f. The formation energy determines the equilibrium concentration of impurities or native defects according to the expression

$$c = N_{\text{sites}} \exp^{-E^f/k_B T} \tag{1}$$

where N_{sites} is the number of sites the defect or impurity can be incorporated on, k_B the Boltzmann constant, and T the temperature. Equation (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:

$$E^f(\text{GaN:O}_{\text{N}}^q) = E_{\text{tot}}(\text{GaN:O}_{\text{N}}^q) - \mu_{\text{O}} + \mu_{\text{N}} + qE_F \tag{2}$$

where $E_{\text{tot}}(\text{GaN:O}_{\text{N}}^q)$ is the total energy derived from a calculation for substitutional O, and q is the charge state of the O donor. E_F is the Fermi level. Similar expressions apply to other impurities and to the various native defects. We refer to Refs. 6 and 9 for a more complete discussion of formation energies and their dependence on chemical potentials.

It should be noted that the Fermi level E_F is not an independent parameter, but is determined by the condition of charge neutrality. However, it is informative to plot formation energies as a function of E_F in order to examine the behavior of defects and impurities when the doping level changes. As for the chemical potentials, these are variables which depend on the details of the growth conditions. For ease of presentation, we set these chemical potentials to fixed values in the figures shown below; however, a general case can always be addressed by referring back to Eq. (2). The fixed values we have chosen correspond to Ga-rich conditions [$\mu_{\text{Ga}} = \mu_{\text{Ga(bulk)}}$], and to maximum incorporation of the various impurities, with solubilities determined by equilibrium with Ga_2O_3, Si_3N_4, and Mg_3N_2.

3. NATIVE DEFECTS

Our first-principles results for native defects were described in detail in Ref. 10. One general conclusion is that self-interstitial and antisite defects are high-energy defects in GaN, and are thus unlikely to occur. Nitrogen vacancies (V_{N}) behave as donors, which means that their formation energy is higher in *n*-type material than in *p*-type. Nitrogen vacancies are therefore unlikely to form in *n*-type GaN, and hence they cannot be responsible for *n*-type conductivity – contrary to the conventional wisdom. Indeed, for a long time the nitrogen vacancy was thought to be the source of *n*-type conductivity in GaN.

The low formation energy of V_{N} in *p*-type GaN, however, *does* make it a likely compensating center for acceptor doping, as will be discussed in Section 5.1. 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, as well as in the frequently observed yellow luminescence. Both aspects will be discussed in the next section.

4. *N*-TYPE DOPING

4.1. Cause of Unintentional *n*-type Doping

As-grown GaN often exhibits high levels of *n*-type conductivity. Our results for native defects and impurities relevant for *n*-type doping are summarized in Fig. 1. As discussed in Section 3, nitrogen vacancies have too high a formation energy to be responsible for *n*-type conductivity in GaN. In contrast, Fig. 1 shows that O and Si have relatively

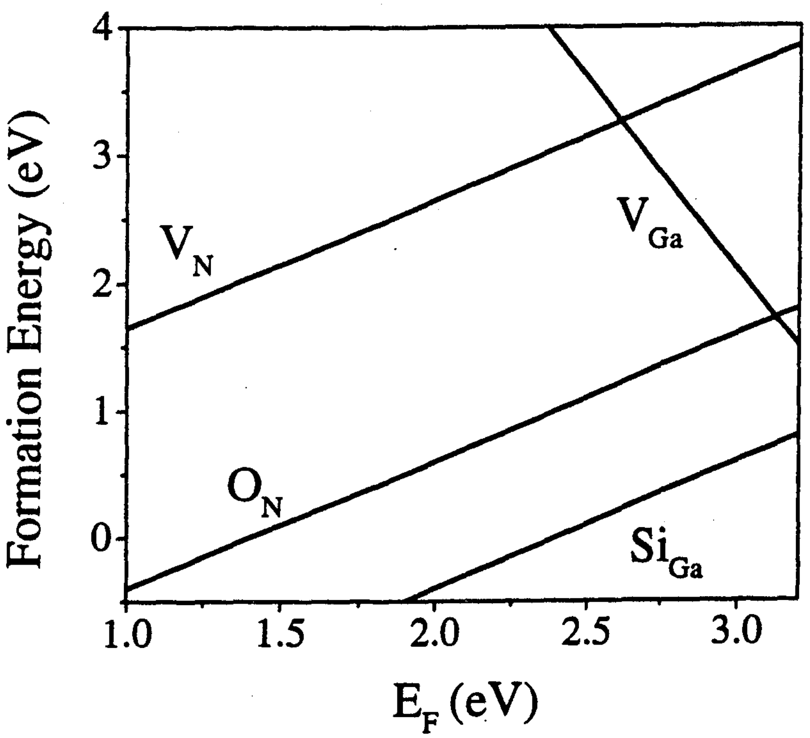

Figure 1. Formation energy *vs.* Fermi energy for native defects (nitrogen and gallium vacancies) and donors (oxygen and silicon) in GaN. The zero of Fermi energy is located at the top of the valence band.

low formation energies in n-type GaN, and can thus be readily incorporated. Both oxygen and silicon form shallow donors in GaN. The slope of the lines in Fig. 1 indicates the charge state of the defect or impurity [see Eq. (2)]: Si_{Ga}, O_N, and V_N all appear with slope +1, indicating single donors.

Oxygen had been considered a potential source of n-type conductivity in GaN by Seifert *et al.*[11] and by Chung and Gershenzon.[12] Still, the prevailing conventional wisdom, attributing the n-type behavior to nitrogen vacancies, proved hard to overcome. Recent experiments have now confirmed that unintentionally doped n-type GaN samples contain silicon or oxygen concentrations high enough to explain the electron concentrations. Götz *et al.*[13] reported electrical characterization of intentionally Si-doped as well as unintentionally doped samples, and concluded that the n-type conductivity in the latter was due to silicon. Götz *et al.* have also recently carried out SIMS (secondary-ion mass spectroscopy) and electrical measurements on hydride vapor phase epitaxy (HVPE) material, finding levels of oxygen or silicon in agreement with the electron concentration.[14]

4.2. Oxygen and Silicon Donors in $Al_xGa_{1-x}N$ Alloys and in GaN under Pressure

High levels of n-type conductivity have always been found in GaN bulk crystals grown at high temperature and high pressure.[15] It has recently been established that the characteristics of these samples (obtained from high-pressure studies) are very similar to epitaxial films which are intentionally doped with oxygen.[16,17] The n-type conductivity of bulk GaN can therefore be attributed to unintentional oxygen incorporation. The high-pressure experiments have also shown that freezeout of carriers occurs at pressures exceeding 20 GPa.[15,17-19] Originally this observation was interpreted as consistent with the presence of nitrogen vacancies,[15] since the V_N donor gives rise to a resonance in the conduction band, which emerges into the band gap under pressure. However, the observations are also entirely consistent with a "*DX*-like" behavior of the oxygen donor.

We have carried out extensive calculations for oxygen in GaN under pressure, as well as in AlGaN alloys.[20] Under compression the oxygen impurity assumes an off-center configuration: a large outward relaxation introduces a deep level in the band gap.[21] This behavior explains the carrier freezeout in GaN under pressure. Silicon donors do not exhibit this transition, consistent with experiment.[19] Alloying with AlN increases the band gap similar to

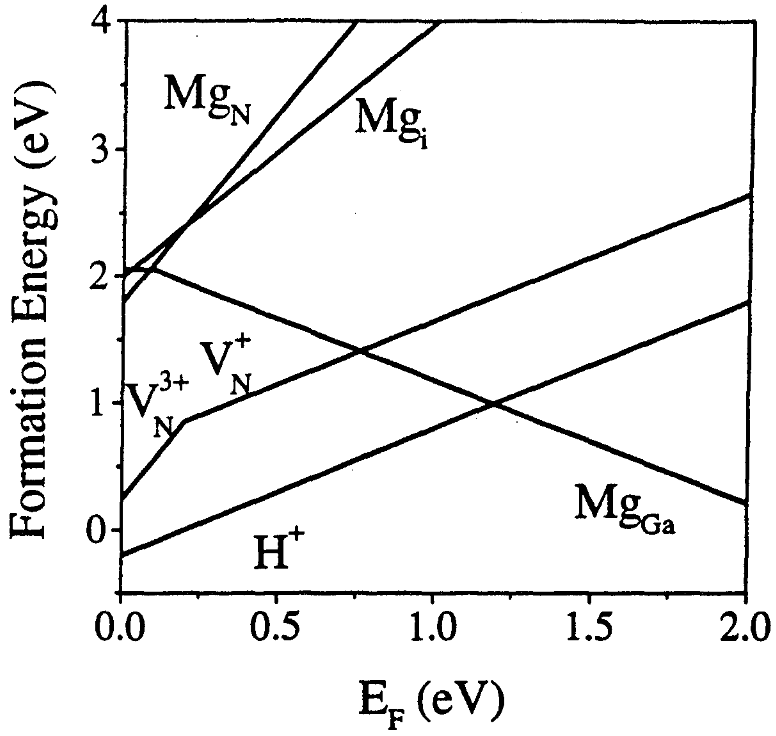

Figure 2. Formation energy as a function of Fermi level for Mg in different configurations (Ga-substitutional, N-substitutional, and interstitial configuration). Also included are the native defects and interstitial hydrogen.

the application of hydrostatic pressure; one therefore expects that the behavior of the impurities in AlGaN would be similar to that in GaN under pressure. Explicit calculations for oxygen in AlN indeed produce DX behavior.[20] These results are consistent with the observed decrease in n-type conductivity of unintentionally doped $Al_xGa_{1-x}N$ as $x > 0.4$.[22]

4.3. Gallium Vacancies and the Yellow Luminescence

Figure 1 also shows, finally, that gallium vacancies (V_{Ga}^{3-}) have relatively low formation energies in highly doped n-type material (E_F high in the gap); they could therefore act as compensating centers. Yi and Wessels[23] have found evidence of compensation by a triply charged defect in Se-doped GaN. We have also proposed that gallium vacancies are responsible for the "yellow luminescence" (YL) in GaN, a broad luminescence band centered around 2.2 eV.[24] The origins of the YL have been extensively debated; as discussed in Refs. 24 and 25, the calculated properties of the gallium vacancy are in good agreement with experimental results for the YL.

5. *P*-TYPE DOPING

Magnesium has emerged as the acceptor dopant of choice in GaN. It has been found, however, that hole concentrations obtained with Mg doping are limited; this is an important barrier to obtaining low-resistance cladding layers and ohmic contacts. In addition, it is well known that Mg-doped GaN grown by MOCVD needs to be subjected to post-growth treatments such as low-energy electron-beam irradiation[26] or thermal annealing[27] in order to activate the acceptors. All of these features can be addressed by our first-principles results, which are summarized in Fig. 2.

We first discuss the behavior of Mg. Then we address the role of hydrogen in p-type GaN. We also report results for alternative acceptors, and discuss doping difficulties in AlGaN alloys.

5.1. Magnesium Acceptors

Our investigations[28] have revealed that hole concentrations in Mg-doped GaN are limited due to the solubility of Mg in GaN, which is determined by competition between incorporation of Mg acceptors and formation of Mg_3N_2. It would be interesting to investigate experimentally whether traces of Mg_3N_2 can be found in highly Mg-doped GaN. Mg prefers the substitutional Ga site, and incorporation of Mg on substitutional N sites (Mg_N) or on interstitial sites (Mg_i) was found to be unfavorable. These features are illustrated in Fig. 2.

Other potential sources of compensation are also illustrated in Fig. 2. The nitrogen vacancy, which had a high formation energy in n-type GaN (see Fig. 1), has a significantly lower formation energy in p-type material, and could act as a compensating center. Figure 2 shows that V_N can occur in a 3+ as well as a + charge state; the +/3+ transition is characterized by a large lattice relaxation.[10] Compensation by nitrogen vacancies may therefore be responsible for the observed persistent photoconductivity effects.[29] The metastability is associated with the different position of the A_1 state near the valence band in the +1 and +3 charge states; this state is occupied with two electrons the +1 charge state, and empty for the 3+ charge state.

Figure 2 also shows that hydrogen, when present, has a formation energy much lower than that of the nitrogen vacancy. It is therefore important to investigate the behavior of H in GaN, which is discussed in the following section.

5.2. Role of Hydrogen in p-type Doping

Hydrogen has strong effects on the properties of GaN. Many growth techniques, such as metal-organic chemical vapor deposition (MOCVD) or hydride vapor phase epitaxy (HVPE) introduce large concentrations of hydrogen in the growing material. The behavior of hydrogen in GaN was analyzed in detail in Refs. 31 and 32. We found that hydrogen incorporates more readily in p-type than in n-type GaN. In p-type GaN H behaves as a donor (H^+), compensating acceptors. Hydrogen can bind to the Mg acceptors with a binding energy of 0.7 eV. The structure of the resulting complex is unusual in that H does not sit next to the magnesium atom, but actually binds to a nitrogen atom which is a neighbor of the acceptor. As a direct consequence the vibrational frequency of the complex is *not* representative of a Ga-H bond, but rather of a N-H bond. The calculated vibrational frequency is 3360 cm^{-1}. Götz *et al.*[33] have reported a value of 3125 cm^{-1} for this local vibrational mode.

The formation energy of hydrogen in p-GaN, as shown in Fig. 2, is much lower than that of the nitrogen vacancy. In growth situations where hydrogen is present (such as MOCVD or HVPE) Mg-doped material will therefore preferentially be compensated by hydrogen, and compensation by nitrogen vacancies will be suppressed. In addition, the incorporation of hydrogen actually increases the incorporation of acceptor dopants.[32] The presence of hydrogen is thus beneficial - at the expense, of course, of obtaining material that is heavily compensated by hydrogen! Fortunately, the hydrogen can be removed from the active region by treatments such as low-energy electron-beam irradiation[26] or thermal annealing.[27]

We have recently also studied the interactions of hydrogen with native point defects in GaN.[30] Since antisites and self-interstitials are very unlikely to form in GaN (see Section 3) we have 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 center 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 $(V_N H)^{2+}$ 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 Fig. 2. We have proposed[30] that this complex is involved in the appearance and disappearance of photoluminescence (PL) lines during post-growth annealing of Mg-doped layers grown by MOCVD.[34]

5.3. Alternative Acceptors

For magnesium we concluded that achievable doping levels are mainly limited by the solubility of Mg in GaN. We have investigated other candidate acceptor impurities, and evaluated them in terms of solubility, shallow *vs.* deep character, and potential compensation due to incorporation on other sites.[35,36] None of the candidate impurities exhibited characteristics exceeding those of Mg. The only acceptor which has a slightly higher solubility than Mg is Be. However, doping with Be may be complicated due to the fact that the small Be atom easily incorporates on interstitial sites, where it acts as a donor, thus causing self-compensation.

5.4. Doping of $Al_xGa_{1-x}N$ Alloys

We have carried out similar calculations for the formation energy of native defects and impurities in AlN.[37] The nitrogen vacancy has a strikingly lower formation energy in AlN than in GaN; it will therefore introduce more severe compensation. We propose that compensation by nitrogen vacancies is the likely cause of the decreased doping

Table 1. Experimental lattice constants (a, in Å) and room-temperature band gaps (E_g, in eV) for zincblende AlN, GaN, and InN.

	AlN	GaN	InN
a	4.37	4.50	4.98
E_g	6.20	3.39	1.89

efficiency of Mg when the Al content is raised in $Al_xGa_{1-x}N$ alloys. In addition, we find that the acceptor ionization energy increases with increasing Al content in $Al_xGa_{1-x}N$ alloys, rising from 200 meV in GaN to 400 meV in AlN.

6. HETEROJUNCTIONS

Heterojunctions are essential for most optoelectronic devices, to provide carrier as well as optical confinement. Most nitride-based devices incorporate heterojunctions between GaN, AlN, or InN, or their alloys. The most important parameters characterizing such heterojunctions are the band discontinuities in the conduction and valence bands. It is well known that these band offsets sensitively depend on the strain condition of the materials joined at the interface; however, these strains have not always been properly taken into account in the analysis of experimental data or computational results.

Table 1 lists lattice constants and band gaps for the nitrides (in the zincblende phase). The lattice mismatch between AlN and GaN is about 3%; between GaN and InN, the mismatch is over 11%. The band offsets are only well defined in the case of a pseudomorphic interface, in which the materials on either side of the junction are strained in order to match a common in-plane lattice constant. For instance, when InN is grown on a thick layer of GaN, the InN should be compressed in the plane of the interface to match the GaN lattice constant, and expanded in the perpendicular direction (by a factor determined by Poisson's ratio). The critical layer thickness (beyond which dislocation formation sets in and the interface is no longer pseudomorphic) for growth of pure InN on GaN is probably very small, but the same logic applies for growth of InGaN alloys on GaN. Results for alloys can usually be obtained by linear interpolation.

Our computations focused on (110) interfaces between the nitrides in the zincblende phase. We expect very little difference for the wurtzite phase, which differs from zincblende only in the atomic arrangements beyond third nearest neighbors. We also expect only minor changes for other interface orientations.

We used a superlattice geometry in the calculations, and various values of the in-plane lattice constant. The materials are strained according to their elastic constants, and relaxation of the atoms around the interface is explicitly allowed. The superlattice calculation yields the lineup of average electrostatic potentials across the interface; the position of the valence-band maximum with respect to the average electrostatic potential is obtained from bulk calculations.[38]

Instead or re-calculating the bulk electronic structure for every strain situation, we have derived *deformation potentials* describing the changes in band edges due to various strain components. We have also calculated the *absolute* deformation potentials for the valence-band maximum. Using the band lineups at strained interfaces together with the deformation potentials allows us to derive a so-called *natural* band lineup between unstrained materials. This natural band lineup can be used as a starting point to calculate offsets at an arbitrary interface, by using information about the strains and the deformation potentials. More information about deformation potentials was published in Ref. 39.

The natural band lineups for the nitrides are illustrated in Fig. 3. the valence-band offset between AlN and GaN (for which the lattice mismatch is relatively modest) is about 0.7 eV, consistent with other recent determinations.[40–42] For GaN/InN we find a surprisingly small offset, 0.3 eV. Atomic relaxations play an important role at this interface, driving the valence-band offset toward lower values. The low value of this offset implies a lack of hole confinement in GaN/InGaN quantum wells.

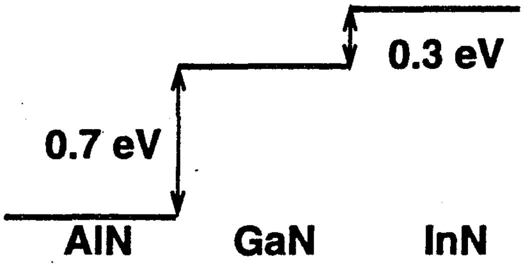

Figure 3. Natural valence-band lineups between AlN, GaN, and InN, obtained from first-principles calculations for zincblende (110) interfaces.

7. CONCLUSIONS

The rapid progress in development of nitride-based devices requires a fundamental understanding of the materials properties, including behavior of point defects, dopants, and interfaces. First-principles calculations can greatly assist in providing a framework for understanding doping problems. Specific results for donor and acceptor doping have been presented in this paper. The main conclusions for n-type GaN are:

- Nitrogen vacancies are *not* responsible for unintentional n-type conductivity.
- Silicon and oxygen donors can be incorporated in large concentrations, likely causing unintentional n-type doping.
- Oxygen (but not silicon) behaves as a DX center in GaN under pressure and in AlGaN alloys.
- Gallium vacancies are the likely source of the yellow luminescence.

For p-type GaN we found that:

- Magnesium is still the acceptor of choice.
- The resulting hole concentration is limited due to Mg solubility.
- Incorporation of Mg on interstitial sites or antisites is not a problem.
- Hydrogen has a beneficial effect on p-type doping because it suppresses compensation and enhances acceptor incorporation.
- Compensation by nitrogen vacancies may occur, likely causing the observed persistent photoconductivity.
- Compensation by nitrogen vacancies becomes worse as x increases in $Al_xGa_{1-x}N$ alloys.

Finally, we have investigated interfaces between the III-V nitrides and reported results for natural band lineups.

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REFERENCES

1. For a recent review, see F. A. Ponce and D. P. Bour, *Nature* **386** (1997) 351.
2. P. Hohenberg and W. Kohn, *Phys. Rev.* **136**, B864 (1964); W. Kohn and L. J. Sham, *ibid.* **140**, A1133 (1965).
3. N. Troullier and J. L. Martins, *Phys. Rev. B* **43**, 1993 (1991).
4. S. G. Louie, S. Froyen, and M. L. Cohen, *Phys. Rev. B* **26**, 1738 (1982).
5. J. Neugebauer and C. G. Van de Walle, *Proc. Mater. Res. Soc. Symp.* **339**, 687 (1994).
6. J. Neugebauer and C. G. Van de Walle, *Phys. Rev. B* **50**, 8067 (1994).
7. R. Stumpf and M. Scheffler, *Comp. Phys. Commun.* **79**, 447 (1994).
8. J. Neugebauer and C. G. Van de Walle, *Proc. Mater. Res. Soc. Symp.* **408** (1996).
9. C. G. Van de Walle, D. B. Laks, G. F. Neumark, and S. T. Pantelides, *Phys. Rev. B* **47**, 9425 (1993).
10. J. Neugebauer and C. G. Van de Walle, in *Festkörperprobleme/Advances in Solid State Physics*, Vol. **35**, ed. R. Helbig (Vieweg, Braunschweig/Wiesbaden), p. 25 (1996).
11. W. Seifert, R. Franzheld, E. Butter, H. Sobotta, and V. Riede, *Cryst. Res. & Technol.* **18**, 383 (1983).
12. B.-C. Chung and M. Gershenzon, *J. Appl. Phys.* **72**, 651 (1992).
13. W. Götz, N. M. Johnson, C. Chen, H. Liu, C. Kuo, and W. Imler, *Appl. Phys. Lett.* **68**, 3114 (1996).
14. W. Götz , J. Walker, L. T. Romano, and N. M. Johnson, *Proc. Mater. Res. Soc. Symp.* **449**, 525 (1997).
15. P. Perlin, T. Suski, H. Teisseyre, M. Leszczyński, I. Grzegory, J. Jun, S. Porowski, P. Boguslawski, J. Bernholc, J. C. Chervin, A. Polian, and T. D. Moustakas, *Phys. Rev. Lett.* **75**, 296 (1995).
16. C. Wetzel, T. Suski, J. W. Ager III, W. Walukiewicz, S. Fisher, B. K. Meyer, I. Grzegory, and S. Porowski, *Proc. ICPS-23* (World Scientific, Singapore), p. 2929 (1996).
17. P. Perlin, T. Suski, A. Polian, J. C. Chervin, W. Knap, J. Camassel, I. Grzegory, S. Porowski and J. W. Erickson, *Proc. Mater. Res. Soc. Symp.* **449**, 519 (1997).
18. C. Wetzel, W. Walukiewicz, E. E. Haller, J. W. Ager III, I. Grzegory, S. Porowski, and T. Suski, *Phys. Rev. B* **53**, 1322 (1996).
19. C. Wetzel, T. Suski, J. W. Ager III, E. R. Weber, E. E. Haller, S. Fischer B. K. Meyer, R. J. Molnar, and P. Perlin, *Phys. Rev. Lett.* **78**, 3923 (1997).
20. C. G. Van de Walle, *Phys. Rev. B* (Jan. 15, 1998).
21. D. J. Chadi and K. J. Chang, *Phys. Rev. Lett.* **61**, 873 (1988).
22. H. G. Lee, M. Gershenzon, and B. L. Goldenberg, *J. Electron. Mat.* **20**, 621 (1991).
23. G.-C. Yi and B. W. Wessels, *Appl. Phys. Lett.* **69**, 3028 (1996).
24. J. Neugebauer and C. G. Van de Walle, *Appl. Phys. Lett.* **69**, 503 (1996).
25. C. G. Van de Walle and J. Neugebauer, *Proc. Mater. Res. Soc. Symp.* **449** (1997) 861.
26. H. Amano, M. Kito, K. Hiramatsu, and I. Akasaki, *Jpn. J. Appl. Phys.* **28** (1989) L2112.
27. S. Nakamura, N. Iwasa, M. Senoh, and T. Mukai, *Jpn. J. Appl. Phys.* **31** (1992) 1258.
28. J. Neugebauer and C. G. Van de Walle, *Proc. Mater. Res. Soc. Symp.* **395**, 645 (1996).
29. C. Johnson, J. Y. Lin, H. X. Jiang, M. A. Khan, and C. J. Sun, *Appl. Phys. Lett.* **68** (1996) 1808; J. Z. Li, J. Y. Lin, H. X. Jiang, A. Salvador, A. Botchkarev, and H. Morkoc, *ibid.* **69** (1996) 1474.
30. C. G. Van de Walle, *Phys. Rev. B* **56**, R10 020 (1997).
31. J. Neugebauer and C. G. Van de Walle, *Phys. Rev. Lett.* **75**, 4452 (1995).
32. J. Neugebauer and C. G. Van de Walle, *Appl. Phys. Lett.* **68**, 1829 (1996).
33. W. Götz, N. M. Johnson, J. Walker, D. P. Bour, M. D. McCluskey, and E. E. Haller, *Appl. Phys. Lett.* **68** (1996) 3725.
34. W. Götz, N. M. Johnson, J. Walker, D. P. Bour, and R. A. Street, *Appl. Phys. Lett.* **68**, 667 (1996).
35. J. Neugebauer and C. G. Van de Walle, *Proc. ICPS-23* (World Scientific, Singapore, 1996) p. 2849.
36. J. Neugebauer and C. G. Van de Walle (unpublished).
37. C. Stampfl and C. G. Van de Walle, *Appl. Phys. Lett.* **72** (Jan. 26, 1998).
38. A. Franciosi and C. G. Van de Walle, *Surface Science Reports* Vol. 25, Nos. 1-4, pp. 1-140 (1996).
39. C. G. Van de Walle and J. Neugebauer, *Appl. Phys. Lett.* **70**, 2577 (1997).
40. G. Martin, A. Botchkarev, A. Rockett, and H. Morkoç, *Appl. Phys. Lett.* **68**, 2541 (1996).
41. E. A. Albanesi, W. R. L. Lambrecht, and B. Segall, *J. Vac. Sci. Technol. B* **12**, 2470 (1994).
42. X. Chen, X. Hua, J. Hu, J.-M. Langlois, and W. A. Goddard III, *Phys. Rev. B* **53**, 1377 (1996).