Mat. Sci. Forum 338-342, 1561 (2000)

Theory of impurities and defects in III-nitrides: vacancies in GaN and related materials

Chris G. Van de Walle[1,*]

[1]Fritz-Haber-Institut, Abt. Theorie, Faradayweg 4–6, D-14195 Berlin, Germany, and
Paul-Drude-Institut, Hausvogteiplatz 5-7, D-10117 Berlin, Germany
*Permanent address: Xerox Palo Alto Research Center, Palo Alto, California 94304, USA
e-mail: vandewalle@parc.xerox.com

Keywords: first-principles calculations, doping, impurities, oxygen, vacancies

Abstract We review a theoretical approach for studying defects and impurities in wide-band-gap semiconductors, focusing on mechanisms that limit doping. Among native defects, vacancies play a prominent role. They cause compensation, and also give rise to luminescence bands. The behavior of gallium and nitrogen vacancies in GaN is compared with cation and anion vacancies in other wide-band-gap semiconductors, including ZnO.

1. Introduction

The III-nitride semiconductors are widely recognized as excellent materials for a wide range of electronic and optoelectronic devices, including light emitters, detectors, and transistors for high-temperature, high-power, and high-frequency applications. The ability to control doping is crucial for all of these applications; wide-band-gap semiconductors such as GaN have long suffered from lack of control of p-type and/or n-type doping. 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.

Among the various types of native point defects, only *vacancies* are low enough in energy to form in significant concentrations. Nitrogen vacancies are *not* responsible for the n-type conductivity of as-grown GaN; however, they do act as donors and compensate p-type GaN. We will discuss similarities and differences with anion vacancies in other III-V and II-VI compounds, including ZnO. Gallium vacancies act as acceptors and form a source of compensation in n-type GaN. Furthermore, we have proposed the gallium vacancy to be the source of the "yellow luminescence". Again, we will draw comparisons with other wide-band-gap semiconductors, including ZnO, where we suggest Zn vacancies to be the cause of the "green luminescence".

Section 2 contains a brief description of the theoretical approach. In Section 3 we will discuss results for anion vacancies: V_{N} in the nitrides, and V_{O} in ZnO. Section 4 contains our results for cation vacancies : V_{Ga} or V_{Al} in the nitrides, and V_{Zn} in the II-VI compounds.

2. Theoretical approach

The key parameters in our approach are obtained from first-principles calculations that do not require any adjustable parameters nor any input from experiment. The computations are founded on density-functional theory, using a supercell geometry and soft pseudopotentials. Details of the computational approach can be found in Refs. [1] and [2].

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 $c = N_{\text{sites}} \exp(-E^f/k_B T)$, 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. It is clear 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:

$$E^f(\text{GaN:O}_{\text{N}}^q) = E_{\text{tot}}(\text{GaN:O}_{\text{N}}^q) - \mu_{\text{O}} + \mu_{\text{N}} + qE_F \tag{1}$$

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. [1] and [3] for a more complete discussion of formation energies and their dependence on chemical potentials.

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. Results relevant for the present discussion are depicted in Figure 1. For ease of presentation, we have set the chemical potentials equal to fixed values; however, a general case can always be addressed by referring back to Eq. (1). 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_2N_3. For each defect we only show the line segment corresponding to the charge state that gives rise to the lowest energy at a particular value of E_F. The change in slope of the lines therefore represents a change in the charge state of the defect [see Eq. (1)], and the Fermi-level position at which this change occurs corresponds to a transition level that can be experimentally measured.

3. Anion vacancies

3.1 Nitrogen vacancies in GaN

Our first-principles results for native defects show that self-interstitials and antisites are high-energy defects in GaN, and are thus unlikely to occur [1, 4]. Nitrogen vacancies (V_{N}) behave as donors, as seen in Fig. 1: the formation energy of V_{N} exhibits a slope of +1 [see Eq. (1)]. The formation energy of V_{N} is very high in n-type material; V_{N} are therefore unlikely to form in n-type GaN, and hence they cannot be responsible for n-type conductivity.

We have proposed that unintentional impurities such as oxygen and silicon are the actual cause of the observed unintentional n-type doping [5]. Figure 1 shows that O and Si are shallow donors with formation energies much lower than V_{N}; they will therefore readily incorporate during growth. Support for this assignment has come from SIMS studies [6] as well as from high-pressure studies [7]. The latter have shown that oxygen (but not Si) behaves as a *DX* center in GaN under pressure [8], in agreement with theoretical predictions [9].

Figure 1 shows that the formation energy of V_{N} is significantly lowered in p-type GaN, making it a likely compensating center in case of acceptor doping. Compensation by V_{N} is suppressed when hydrogen is present [10], i.e., in growth techniques such as MOCVD or HVPE. Figure 1 also shows that V_{N} can occur in a 3+ as well as a + charge state, with a transition level within

0.5 eV of the top of the valence band. V_N may therefore be responsible [11, 12] for the blue lines commonly observed by photoluminescence in Mg-doped GaN [13, 14, 15, 16].

Nitrogen vacancies may also be responsible for the persistent photoconductivity effects that have often been observed in *p*-type GaN [13]. The +/3+ transition of V_N is characterized by a large lattice relaxation [4]. Such large differences in relaxation are usually indicative of metastability, which can produce persistent photoconductivity. Here 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. The 2+ charge state is always higher in energy than either 1+ or 3+, and thus thermodynamically never stable; this is characteristic of a so-called "negative-U defect".

Finally, we note that the appearance and disappearance of photoluminescence (PL) lines during post-growth annealing of Mg-doped layers grown by MOCVD [17, 18] may be related to the interactions of H with V_N. Complexes between hydrogen and nitrogen vacancies can form during growth [12]; the calculated binding energy of the $(V_N\text{-H})^{2+}$ complex, expressed with respect to interstitial H^+, is 1.56 eV. Dissociation of this complex, producing isolated nitrogen vacancies, may explain the behavior of PL lines during annealing for acceptor activation.

3.2 Nitrogen vacancies in AlGaN

The behavior of V_N in AlN is qualitatively very similar to GaN [19]. However, the +/3+ level occurs at a higher position in the band gap in the case of AlN (around 1 eV, consistent with a roughly constant position of this deep level across the GaN/AlN interface, assuming a valence-band offset of 0.7 eV). Because the formation energy decreases much faster with decreasing E_F in the 3+ charge state, V_N becomes much more favorable for low Fermi-level positions in AlN.

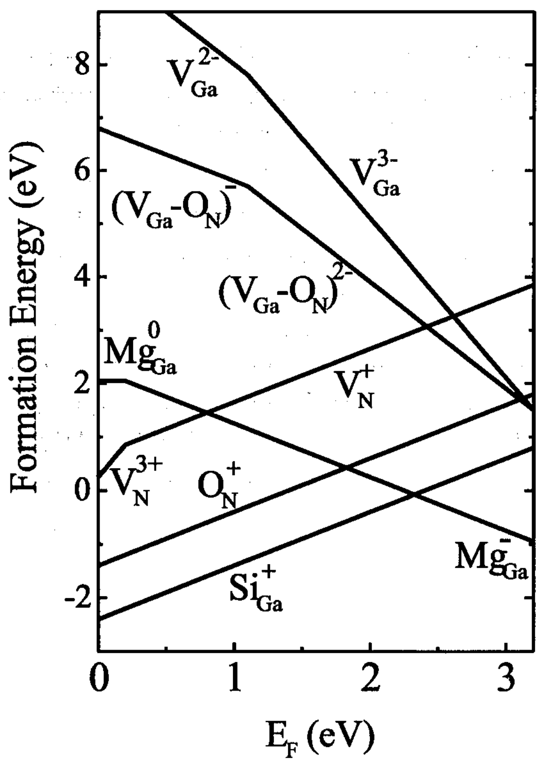

Figure 1: Formation energy *vs.* Fermi energy for important native defects and impurities in GaN. The zero of E_F is located at the top of the valence band, and Ga-rich conditions are assumed.

3.3 Anion vacancies in other compounds

Anion vacancies in compound semiconductors tend to behave as donors, and thus compensate *p*-type material. The negative-U character and large lattice relaxation have also been observed for the As vacancy in GaAs [20]. One may wonder why V_N in GaN behaves as a shallow donor, while V_{As} in GaAs only gives rise to deep levels. The explanation lies in the significantly smaller lattice constant of GaN. When an anion vacancy is formed, four deep levels are introduced in the band gap which arise from the four dangling bonds on the neighboring cations. In the neutral charge state, three electrons need to be accommodated in these levels (since each Ga dangling bond contributes 3/4 electron). In GaAs, the Ga neighbors are far enough apart to only weakly interact; but in GaN, the Ga atoms are much closer together, and their strong interaction leads to a large splitting of the defect levels [1]: three states (occupied with one electron) are pushed above the conduction-band minimum (giving rise to the shallow-donor character), while the symmetric A_1 state, occupied with two electrons, is pushed close to the valence band.

The negative-U behavior is also observed for anion vacancies in II-VI compounds, e.g., for the Se vacancy in ZnSe [21]. Here, however, each dangling bond on the neighboring Zn atoms only contributes 1/2 electron, leading to a total of two electrons to be accommodated in the defect levels; both of these are accommodated in the A_1 state. This picture immediately makes clear why the oxygen vacancy in ZnO does not behave as a shallow donor, contrary to what has often been assumed. Recent first-principles calculations [22] have indeed shown that V_O has a 2+/0 transition level deep in the band gap. Again, the 1+ charge state is unstable, characteristic of a negative-U center.

4. Cation vacancies

4.1 Gallium vacancies in GaN

Figure 1 shows that gallium vacancies (V_{Ga}^{3-}) have relatively low formation energies in highly doped n-type material; they could therefore act as compensating centers. Yi and Wessels [23] found evidence of compensation by a triply charged defect in Se-doped GaN.

We have proposed that gallium vacancies are responsible for the "yellow luminescence" (YL) in GaN, a broad luminescence band centered around 2.2 eV [24]. The most direct evidence for involvement of Ga vacancies in YL was provided by positron annihilation measurements [25], showing that the concentration of V_{Ga} correlates with the intensity of the YL. Here we briefly review other evidence supporting the assignment of the YL to V_{Ga}; further references to experiment can be found in Ref. [26].

Position of the defect level. Figure 1 shows that the Ga vacancy has a deep level (the 2-/3- transition level) about 1.1 eV above the valence band. Transitions between the conduction band (or shallow donors) and this deep level therefore exhibit the correct energy to explain the YL. Various experiments have linked the YL with a deep level located about 1 eV above the valence band [27, 28]. In addition, the calculated pressure dependence of this level is also consistent with experiment [27]. It is noteworthy that the absorption corresponding to this defect level occurs at a significantly higher energy than the emission; in photoluminescence excitation a broad absorption peak around 2.8 eV was observed [29].

n-type *vs.* p-type. The formation energy of V_{Ga}^{3-} shown in Fig. 1 indicates that the defect will mostly form in n-type material. Experiments have indeed indicated a suppression of the YL in p-type material [30].

Complexing with donor impurities. Figure 1 shows that the formation energy of V_{Ga}-O_N complexes is lower than that of the isolated V_{Ga}. We therefore expect an increase in the YL when oxygen is present. The YL intensity indeed increases in the neighborhood of the interface with a sapphire substrate [29], where the oxygen concentration is also known to be higher [6].

4.2 Cation vacancies in AlGaN

The formation energy of cation vacancies in AlN is lower than in GaN [19]; these vacancies thus form an increasingly important source of compensation in $Al_xGa_{1-x}N$ alloys with higher x. This compensation mechanism competes with DX-center formation [9]: oxygen becomes a deep level (and effectively behaves as an acceptor) when $x > 0.3$. Whether Si forms a DX level at high x is still controversial; if it does not, then compensation by cation vacancies will be the dominant compensation mechanism in the absence of oxygen.

As might be expected, the 2-/3- transition level also shifts higher in the band gap in AlN [31], in agreement with the observed "violet luminescence" [32].

4.3 Role of cation vacancies in diffusion

Phase separation in InGaN quantum wells has been a topic of intense debate. McCluskey *et al.* [33] observed that $In_{0.27}Ga_{0.73}N$ quantum wells exhibited significant phase separation after annealing at 950°C for 8 hours. A broad optical absorption peak around 2.65 eV was found in the annealed material. This peak is reminiscent of the absorption found in Ref. [29] in samples with strong YL, which we attributed to Ga vacancies. We interpret the peak observed in Ref. [33] as evidence for the presence of cation vacancies, which are mediating the diffusion process leading to phase separation.

4.4 Cation vacancies in II-VI compounds

Metal vacancies and their complexes with donor impurities (the so called *SA* (self-activated) centers) are well known in II-VI compounds (e.g., ZnS, ZnSe); similar to cation vacancies in III-nitrides, they act as compensating centers in *n*-type material. These defects also 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 [34, 35].

Our calculations for ZnO [22] show that V_{Zn} behaves as an acceptor with a 1-/2- level occurring around 0.8 eV above the valence band. Transitions from electrons in the conduction band to the V_{Zn} level may therefore be responsible for the "'green luminescence" which is frequently observed in ZnO, and is centered between 2.4 and 2.5 eV [36].

Acknowledgements

I gratefully acknowledge fruitful collaborations with J. Neugebauer, C. Stampfl, A. F. Kohan, and G. Ceder, and the support of the Alexander von Humboldt Foundation through a *US Senior Scientist Award.*

References

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

[2] M. Bockstedte, A. Kley, J. Neugebauer, and M. Scheffler, Comp. Phys. Commun. **107** (1997), p. 187.

[3] C. G. Van de Walle, D. B. Laks, G. F. Neumark, and S. T. Pantelides, Phys. Rev. B **47** (1993), p. 9425.

[4] J. Neugebauer and C. G. Van de Walle, in Festkörperprobleme/Advances in Solid State Physics, Vol. **35** (1996), ed. R. Helbig (Vieweg, Braunschweig/Wiesbaden), p. 25.

[5] J. Neugebauer and C. G. Van de Walle, Proc. ICPS-22 (1995) (World Scientific, Singapore), p. 2327.

[6] W. Götz, J. Walker, L. T. Romano, and N. M. Johnson, Mat. Res. Soc. Symp. Proc. **449** (1997), p. 525.

[7] 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** (1995), p. 296.

[8] 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** (1997), p. 3923.

[9] C. G. Van de Walle, Phys. Rev. B **57** (1998), p. 2033.

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

[11] C. H. Park and D. J. Chadi, Phys. Rev. B **55** (1997), p. 12995.

[12] C. G. Van de Walle, Phys. Rev. B. **56** (1997), p. R10 020.

[13] C. Johnson, J. Y. Lin, H. X. Jiang, M. A. Khan, and C. J. Sun, Appl. Phys. Lett. **68** (1996), p. 1808; J. Z. Li, J. Y. Lin, H. X. Jiang, A. Salvador, A. Botchkarev, and H. Morkoc, *ibid.* **69** (1996), p. 1474.

[14] U. Kaufmann, M. Kunzer, M. Maier, H. Obloh, A. Ramakrishnan, B. Santic, and P. Schlotter, Appl. Phys. Lett. **72** (1998), p. 1326.

[15] M. Leroux, B. Beaumont, N. Grandjean, P. Lorenzini, S. Haffouz, P. Venngus, J. Massies, and P. Gibart, Mater. Sci. Engin. B **50** (1997), p. 97.

[16] F. Calle, E. Monroy, F. J. Snchez, E. Muñoz, B. Beaumont, S. Haffouz, M. Leroux, and P. Gibart, MRS Internet J. Nitride Semicond. Res. **3** (1998), p. 24.

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

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

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

[20] J. E. Northrup and S. B. Zhang, Phys. Rev. B **50** (1994), p. 4962.

[21] A. García and J. E. Northrup, Phys. Rev. Lett. **74** (1995), p. 1131.

[22] A. F. Kohan, G. Ceder, and C. G. Van de Walle (unpublished).

[23] G.-C. Yi and B. W. Wessels, Appl. Phys. Lett. **69** (1996), p. 3028.

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

[25] K. Saarinen, T. Laine, S. Kuisma, J. Nissilä, P. Hautojärvi, L. Dobrzynski, J. M. Baranowski, K. Pakula, R. Stepniewski, M. Wojdak, A. Wysmolek, T. Suski, M. Leszczynski, I. Grzegory, and S. Porowski, Phys. Rev. Lett. **79** (1997), p. 3030.

[26] C. G. Van de Walle and J. Neugebauer, in *Properties, Processing and Applications of Gallium Nitride and Related Semiconductors*, edited by J. Edgar, S. Strite, I. Akasaki, H. Amano, and C. Wetzel, EMIS Datareview Series No. 23 (INSPEC, IEE, 1999), pp. 313-316.

[27] T. Suski, P. Perlin, H. Teisseyre, M. Leszczyński, I. Grzegory, J. Jun, M. Boćkowski, and S. Porowski, Appl. Phys. Lett. **67** (1995), p. 2188.

[28] E. Calleja, F. J. Sánchez, D. Basak, M. A. Sánchez-García, E. Muñoz, I. Izpura, F. Calle, J. M. G. Tijero, B. Beaumont, P. Lorenzini, and P. Gibart, Phys. Rev. B **55** (1997), p. 4689.

[29] D. M. Hofmann, D. Kovalev, G. Steude, B. K. Meyer, A. Hoffmann, L. Eckey, R. Heitz, T. Detchprom, H. Amano, and I. Akasaki, Phys. Rev. B **52** (1995), p. 16702.

[30] X. Zhang, P. Kung, D. Walker, A. Saxler, and M. Razeghi, Mat. Res. Soc. Symp. Proc. **395** (1996), p. 625.

[31] T. Mattila and R. M. Nieminen, Phys. Rev. B **55** (1997), p. 9571.

[32] R. A. Youngman and J. H. Harris, J. Am. Ceram. Soc. **73** (1990), p. 3238 and references therein.

[33] M. D. McCluskey, L. T. Romano, B. S. Krusor, D. P. Bour, N. M. Johnson, and S. Brennan, Appl. Phys. Lett. **72** (1998), p. 1730.

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

[35] P. J. Dean, Phys. Stat. Sol. (a) **81** (1984), p. 625.

[36] D. C. Reynolds, D. C. Look, B. Jogai, and H. Morkoç, Solid State Commun. **101** (1997), p. 643.