Defects and doping in GaN

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First-principles calculations for defects and impurities in GaN provide a wealth of information about doping and electronic properties. We have been able to show that nitrogen vacancies are *not* the cause of n-type conductivity in GaN. Results for silicon and oxygen indicate that unintentional incorporation of these impurities is the most plausible explanation for n-type conductivity. For p-type GaN, we find that Mg incorporation is limited by solubility. The role of hydrogen in acceptor-doped material is discussed.

I. Introduction

Gallium nitride has recently emerged as the prime material for the fabrication of green, blue, and ultraviolet light-emitting devices. Light-emitting diodes [1] are already being produced in large quantities, for use in applications ranging from traffic lights to full-color displays. Nakamura and coworkers have also achieved various milestones in the fabrication of laser diodes, including room-temperature CW (continuous wave) operation [2]. In addition, GaN is a very promising material for high-frequency and high-power electronic devices [3] and for solar-blind detectors [4].

In spite of the rapid progress in the field, various aspects of the structural and electronic behavior of GaN are still poorly understood. One such problem is doping. Several years ago we countered the conventional wisdom by suggesting that nitrogen vacancies were *not* responsible for the commonly observed n-type conductivity in GaN [5]. Instead we proposed that donor impurities are unintentionally incorporated, with oxygen and silicon the main candidates for donors in GaN [6]. Our proposals have recently been confirmed in a number of experimental investigations, showing that oxygen and silicon concentrations in well characterized samples are high enough to explain the observed electron concentrations. Our current understanding will be discussed in Sec. III.

Regarding p-type doping, the doping levels are still lower than desirable for low-resistance cladding layers and ohmic contacts. Achieving higher hole concentrations with Mg as the dopant has proved difficult; various explanations have been proposed for this limitation. Our investigations of compensation mechanisms [7] have revealed that the determining factor is the solubility of Mg in GaN, which is limited by competition between incorporation of Mg acceptors and formation of Mg_3N_2. Incorporation of Mg on interstitial or substitutional nitrogen sites was found to be unfavorable. The role of hydrogen during p-type doping and subsequent anneals was addressed in in Refs. [8] and [9]. These issues are discussed in Sec. IV.

II. Theoretical approach

All of our calculations are based on first-principles methods that do not require any adjustable parameters or any input from experiment. The computations are founded on density-functional theory, [10] using a supercell geometry and soft Troullier-Martins pseudopotentials [11]. The effect of d electrons in GaN is taken into account either through the so-called non-linear core correction [12] or by explicit inclusion of the d electrons as valence electrons; the latter proved to be necessary for obtaining accurate results in certain cases [13]. Our results should apply to both the wurtzite and zincblende phases of the nitride semiconductors; indeed, in Ref. 13 we reported that the wurtzite and the cubic phase show nearly equivalent formation energies and electronic structure for defects. Further details of the computational approach can be found elsewhere [5,14,15].

The equilibrium concentration of impurities or native defects is given by

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

where N_{sites} is the number of sites the defect or impurity can be incorporated on, k_B the Boltzmann constant, T the temperature, and E^f the formation energy. Equation (1) shows that defects with a *high* formation energy will occur in *low* concentrations. In principle we should be calculating *free energies*; in practice, the computational effort involved in calculating vibrational entropies exceeds current computational resources. For many purposes, such as the calculation of solubilities, the entropy terms cancel to a large extent. Overall, we are careful to make sure that our derived trends and conclusions are not affected by our approximations.

The formation energy is not a constant but depends on the various growth parameters. 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_0, μ_{Ga} and μ_N. 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 nitrogen atom and the addition of one O atom; the formation energy is therefore:

$$E^f(GaN : O_N^q) = E_{\text{tot}}(GaN : O_N^q) - \mu_0 + \mu_N + qE_F \qquad (2)$$

where $E_{\text{tot}}(\text{GaN:O}_N^q)$ 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. 5 and 16 for a more complete discussion of formation energies and their dependence on chemical potentials.

Note 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 ($\mu_{Ga} = \mu_{Ga(\text{bulk})}$) and to maximum incorporation of the various impurities, with solubilities determined by equilibrium with Ga_20_3, Si_3N_4, and Mg_2N_3.

III. Donors in GaN

We have evaluated a number of candidate donors in GaN. Among the native defects, only the vacancies have low enough formation energies to be incorporated in observable concentrations; self-interstitials and antisites are always high-energy defects [5]. The gallium vacancy behaves as an acceptor, while the nitrogen vacancy is a donor. Similar results for native defects were obtained by Boguslawski et al.[17]. With regard to extrinsic impurities, we have evaluated silicon, oxygen, and carbon. While carbon could in principle behave as a donor when incorporated on the gallium site, the formation energy for this configuration is very high, and much larger than for incorporation of carbon on the nitrogen site, where it acts as an acceptor. We therefore focus on silicon and oxygen, both of which behave as shallow acceptors.

Fig. 1 summarizes our first-principles results for native defects and impurities relevant for n-type doping. We observe that nitrogen vacancies (V_N) have high energies in n-type GaN, and are thus unlikely to occur in significant concentrations. This finding allow us to conclude that nitrogen vacancies are not responsible for n-type conductivity in GaN. In contrast, Fig. 1 shows that oxygen and silicon have relatively 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: $\mathrm{Si_{Ga}}$, O_N and V_N all appear with slope +1, indicating they are single donors.

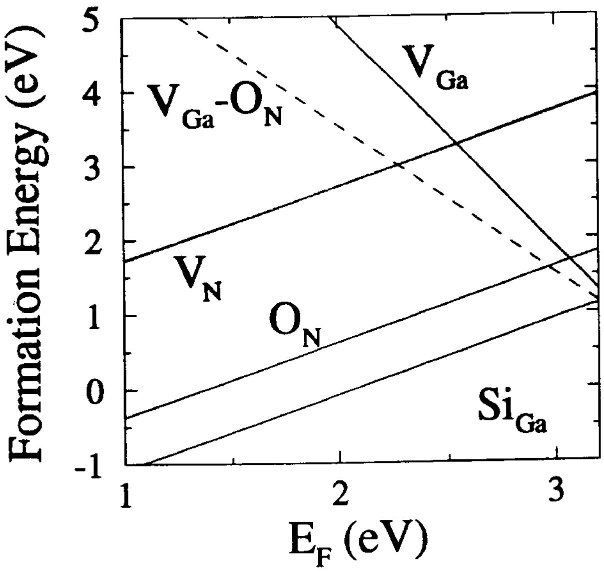

Figure 1. Formation energy vs. Fermi energy for native defects (nitrogen and gallium vacancies), donors (oxygen and silicon) and the V_{Ga-ON} complex. The zero of Fermi energy is located at the top of the valence band.

The suggestion that oxygen can be responsible for n-type conductivity in GaN was made by Seifert et al.[18] and by Chung and Gershenzon [19]. Still, the prevailing conventional wisdom, attributing the n-type behavior to nitrogen vacancies, proved hard to overcome. Recent experiments have confirmed that unintentionally doped n-type GaN samples contain silicon or oxygen concentrations high enough to explain the electron concentrations. Gotz et al.[20] 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. They also found evidence of another shallow donor with a slightly higher activation energy, which was attributed to oxygen. 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 [21].

High levels of n-type conductivity have always been found in GaN bulk crystals grown at high temperature and high pressure [22]. 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 [23,24]. 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 [22,24,25]. Originally this observation was interpreted as consistent with the presence of nitrogen vacancies, 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. Indeed, we find [26] that in GaN under pressure the oxygen impurity assumes an off-center configuration: a large outward relaxation introduces a deep level in the band gap. This behavior explains the carrier freezeout in GaN under pressure. Silicon donors do not exhibit the transition, consistent with experiment. One would expect that the behavior of the impurities in AlN would be similar to that in GaN under hydrostatic pressure, and this is indeed confirmed by explicit calculations [26].

As a final comment on Fig. 1 we note 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 [27] have found evidence of compensation by a triply charged defect in Se-doped GaN. We also point out that we have proposed that gallium vacancies are responsible for the "yellow luminescence" (YL) in GaN, a broad luminescence band centered around 2.2 eV [28]. The origins of this luminescence band have been extensively debated; as discussed in Refs. 28 and 29, the calculated properties of the gallium vacancy are in good agreement with experimental results.

IV. Acceptors in GaN

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. In addition, it is well known that Mg-doped GaN grown by MOCVD (metal-organic chemical vapor deposition) needs to be subjected to post-growth treatments such as low-energy electron-beam irradiation [30] or thermal annealing [31] in order to activate the acceptors. All of these features can be addressed by our first-principles results, which are summarized in Fig. 2.

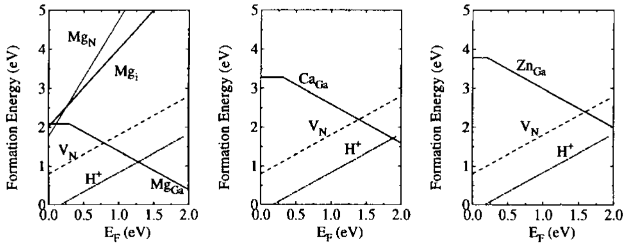

Figure 2. Formation energy as a function of Fermi level for Mg, Ca, and Zn in different configurations (Ga-substitutional, N-substitutional, and interstitial configuration). Also included are the native defects and interstitial H.

The Mg acceptor has a low enough formation energy to be incorporated in large concentrations in GaN. For the purposes of the plot, we have assumed Ga-rich conditions (which are actually the least favorable for incorporating Mg on Ga sites), and equilibrium with Mg_2N_3, which determines the solubility limit for Mg. We note that the formation energies for Mg^0_{Ga} and Mg^-_{Ga} intersect for a Fermi level position around 250 meV; this transition level would correspond to the ionization energy of the Mg acceptor. However, since our calculated formation energies are subject to numerical error bars of ± 0.1 eV, this value should not be taken as an accurate assessment of the ionization energy.

We have also investigated other positions of Mg in the lattice, such as on substitutional N sites (Mg_N) and on interstitial sites (Mg_i), always finding much larger formation energies. We therefore conclude that Mg overwhelmingly prefers the Ga site in GaN, the main competition being with formation of Mg_2N_3, which is the solubility-limiting phase. It would be interesting to investigate experimentally whether traces of Mg_2N_3 can be found in highly Mg-doped GaN.

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 n-type material, and could potentially act as a compensating center. However, we also note that hydrogen, when present, has a formation energy much lower than that of the nitrogen vacancy. In growth situations where hydrogen is present (such as MOCVD or HVPE) Mg-doped material will preferentially be compensated by hydrogen, and compensation by nitrogen vacancies will be suppressed. The presence of hydrogen is therefore beneficial - at the expense, of course, of obtaining material which is heavily compensated by hydrogen! Fortunately, the hydrogen can be removed from the active region by treatments such as low-energy electron-beam irradiation [30] or thermal annealing [31]. A more complete discussion of the role of hydrogen in GaN is given in Refs. 8 and 9.

For Mg, we thus conclude 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 [32]. Partial results for Ca and Zn are shown in Fig. 2. None of the candidate impurities exhibited characteristics exceeding those of Mg. In particular, we perceive no noticeable advantage in the use of Be, which has been suggested as a superior dopant.

Last but not least we note the importance of avoiding any type of contamination during growth of p-type GaN. For instance, the oxygen formation energy shown in Fig. 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. In addition, complex formation between oxygen and magnesium can make oxygen incorporation even more favorable [26].

V. Conclusions

In order to continue the rapid progress in development of GaN-based devices, a fundamental understanding is required of the behavior of point defects and dopant impurities. First-principles calculations can greatly help 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 that nitrogen vacancies are *not* responsible for n-type conductivity in as-grown GaN; that silicon and oxygen donors can be incorporated in large concentrations, likely causing unintentional *n*-type doping; and that gallium vacancies are the likely source of the yellow luminescence. For *p*-type GaN we found that Mg is still the acceptor of choice, even though the resulting hole concentration is limited due to Mg solubility, and that incorporation of Mg on interstitial sites or antisites is not a problem.

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References

1. S. Nakamura M. Senoh, and T. Mukai, Jap. J. Appl. Phys. **32**, L8 (1993).
2. S. Nakamura, M. Senoh, S. Nagahama, N. Iwasa, T. Yamada, T. Matsushita, Y. Sugimoto, and H. Kiyoku, Appl. Phys. Lett. **69**, 4056 (1996).
3. M. A. Khan, Q. Chen, C. J. Sun, J. W. Wang, M. Blasingame, M. S. Shur, and H. Park, Appl. Phys. Lett. **68**, 514 (1996).
4. D. Walker, X. Zhang, P. Kung, A. Saxler, S. Javadpour, J. Xu, and M. Razeghi, Appl. Phys. Lett. **68**, 2100 (1996).
5. J. Neugebauer and C. G. Van de Walle, Phys. Rev. B**50**, 8067 (1994).
6. J. Neugebauer and C. G. Van de Walle, in *Proceedings of the 22th International Conference on the Physics of Semiconductors,* Vancouver, 1994, edited by D. J. Lockwood (World Scientific Publishing; Co Pte Ltd., Singapore), p. 2327.
7. J. Neugebauer and C. G. Van de Walle, in *Gallium Nitride and Related Materials,* edited by R. D. Dupuis, J. A. Edmond, F. A. Ponce, and S. Nakamura, Materials Research Society Symposia Proceedings, Vol. 395 (Materials Research Society, Pittsburgh, Pennsylvania), p. 645.
8. J. Neugebauer and C. G. Van de Walle, Phys. Rev. Lett. **75**, 4452 (1995).
9. J. Neugebauer and C. G. Van de Walle, Appl. Phys. Lett. **68**, 1829 (1996).
10. P. Hohenberg and W. Kohn, Phys. Rev. **136**, B864 (1964); W. Kohn and L. J. Sham, ibid. **140**, A1133 (1965).
11. N. Troullier and J. L. Martins, Phys. Rev. B **43**, 1993 (1991).
12. S. G. Louie, S. Froyen, and M. L. Cohen, Phys. Rev. B **26**, 1738 (1982).
13. J. Neugebauer and C. G. Van de Walle, Proc. Mater. Res. Soc. Symp. **339**, 687 (1994).
14. R. Stumpf and M. Scheffler, Comp. Phys. Commun. **79**, 447 (1994).
15. J. Neugebauer and C. G. Van de Walle, Proc. Mater. Res. Soc. Symp. **408** (1996).
16. C. G. Van de Walle, D. B. Laks, G. F. Neumark and S. T. Pantelides, Phys. Rev. B **47**, 9425 (1993).
17. P. Boguslawski, E. L. Briggs and J. Bernholc, Phys. Rev. B**51**, 17 255 (1995).
18. W. Seifert, R. Franzheld, E. Butter, H. Sobotta, and V. Riede, Cryst. Res. & Technol. **18**, 383 (1983).
19. B.-C. Chung and M. Gershenzon, J. Appl. Phys. **72**, 651 (1992).
20. W. Gotz, N. M. Johnson, C. Chen, H. Liu, C. Kuo, and W. Imler, Appl. Phys. Lett. **68**, 3114 (1996).
21. W. Gotz, J. Walker, L. T. Romano, and N. M. Johnson, in III-V Nitrides, edited by F. A. Ponce, T. D. Moustakas, I. Akasaki, and B. A. Monemar, Materials Research Society Symposia Proceedings, Vol. 449 (Materials Research Society, Pittsburgh, Pennsylvania, 1997), in press.
22. P. Perlin, T. Suski, H. Teisseyre, M. Leszczński, 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).
23. 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, 1996), p. 2929.
24. P. Perlin, T. Suski, A. Polian, J. C. Chervin, W. Knap, J. Camassel, I. Grzegory, S. Porowski and J. W. Erickson, in *III-V Nitrides,* edited by F. A. Ponce, T. D. Moustakas, I. Akasaki, and B. A. Monemar, Materials Research Society Symposia Proceedings, Vol. 449 (Materials Research Society, Pittsburgh, Pennsylvania, 1997), in press.

25. C. Wetzel, W. Walukiewicz, E. E. Haller, J. W. Ager III, I. Grzegory, S. Porowski and T. Suski, Phys. Rev. B**53**, 1322 (1996).
26. C. G. Van de Walle (unpublished).
27. G.-C. Yi and B. W. Wessels, Appl. Phys. Lett. **69**, 3028 (1996).
28. J. Neugebauer and C. G. Van de Walle, Appl. Phys. Lett. **69**, 503 (1996).
29. C. G. Van de Walle and J. Neugebauer, in III-V Nitrides, edited by F. A. Ponce, T. D. Moustakas, I. Akasaki and B. A. Monemar, Materials Research Society Symposia Proceedings, Vol. 449 (Materials Research Society, Pittsburgh, Pennsylvania, 1997), in press.
30. H. Amano, M. Kito, K. Hiramatsu and I. Akasaki, Jpn. J. Appl. Phys. **28**, L2112 (1989).
31. S. Nakamura, N. Iwasa, M. Senoh and T. Mukai, Jpn. J. Appl. Phys. **31**, 1258 (1992).
32. J. Neugebauer and C. G. Van de Walle, in *Proceedings of the 23rd International Conference on the Physics of Semiconductors*, Berlin, 1996, edited by M. Scheffler and R. Zimmermann (World Scientific Publishing Co Pte Ltd., Singapore, 1996). p. 2849.