

Published 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.

ROLE OF DEFECTS AND IMPURITIES IN DOPING OF GaN

Jörg Neugebauer^a and Chris G. Van de Walle
Xerox PARC, 3333 Coyote Hill Road, Palo Alto, CA 94304, USA

We have calculated formation energies and position of the defect levels for all native defects and for a variety of donor and acceptor impurities employing first-principles total-energy calculations. An analysis of the numerical results gives direct insight into defect concentrations and impurity solubilities as a function of growth parameters (temperature, chemical potentials) and into the mechanisms limiting the doping levels in GaN. We show how compensation and passivation by native defects or impurities, solubility issues, and incorporation of dopants on other sites influence the acceptor doping levels.

1 Introduction

GaN has attracted widespread attention for producing highly-efficient blue light-emitting diodes¹ and as a promising candidate for high-temperature or high-power devices. Recent progress in growth techniques and device processing enabled the fabrication of the first prototypes of blue laser diodes. However, despite the rapid progress in the development of GaN-based devices doping is still an important issue. Particularly the lack of high *p*-type doping levels limits the achievable injection currents important for improving laser diodes. One reason why high *p*-type doping levels are difficult to achieve is the high ionization energy characteristic for acceptors in GaN. Magnesium, which is the most commonly used acceptor in GaN, has an acceptor binding energy of about 160 meV² implying that at room temperature the hole concentration is less than 1% of the Mg concentration.

The hole concentration is given by $n_{\text{hole}} = N_{\text{acceptors}} \exp(-E_a/k_b T)$ where $N_{\text{acceptors}}$ is the number of acceptors, E_a the acceptor ionization energy, k_b the Boltzman constant, and T the device temperature. The hole concentration can therefore be increased by: (i) increasing the acceptor concentration, (ii) increasing the device temperature, and (iii) finding new acceptors with a lower ionization energy. Increasing the temperature is a device dependent issue and will not be discussed here. One should, however, keep in mind that increasing the temperature above room temperature commonly *decreases* the carrier mobility.

Decreasing the acceptor ionization energy requires to find new acceptor species. There is some experimental evidence that acceptor levels with a lower

^apresent address: Fritz-Haber-Institut der MPG, Faradayweg 4-6, D-14195 Berlin, Germany

binding energy exist: possible candidates which are discussed in the literature are C,³ Ca,⁴ and Zn.⁵ However, for those elements to be really useful for doping it is essential that sufficiently high acceptor concentrations can be achieved.

In the present paper we will discuss which mechanisms limit the doping levels in GaN. In particular compensation by native defects and impurities, complex formation, solubility issues, and incorporation on unintended sites will be studied. Based on these results we explain why growing in hydrogen-rich conditions is beneficial for acceptor incorporation and how this mechanism can be used to optimize *p*-type doping in GaN. As possible acceptor species Mg (which is the most commonly used acceptor), Zn, and Ca will be investigated.

2 Method

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

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

where N_{sites} is the number of sites the defect can be built in. k_B is the Boltzmann constant and S the vibrational entropy. The vibrational entropy is, at the present stage of our work, not explicitly included, which would be computationally very demanding. Entropy contributions cancel to some extent,⁶ and are small enough not to affect any qualitative conclusions.

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

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

where $\Delta E_{\text{tot}}(\text{GaN:Mg}_{\text{Ga}}^q)$ is the total energy difference derived from a calculation for substitutional Mg and bulk GaN, and q is the charge state of the Mg acceptor. Similar expressions apply to the hydrogen impurity, and to the various native defects. For calculating the total energies we have performed first-principles calculations based on density-functional theory (DFT) using a supercell approach with 32 atoms per cell, a plane-wave basis set with 60 Ry cutoff and soft Troullier-Martins pseudopotentials.⁷ Details of the method and convergence checks can be found elsewhere.^{8,9,10}

3 Compensating centers

3.1 Native defects

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

We find that antisites and interstitials have high formation energies, and are therefore very unlikely to occur in any significant concentration.⁸ The vacancies, however, have lower formation energies. Under conditions of thermodynamic equilibrium, low formation energies are required for the defect to occur in high concentration. In particular, the nitrogen vacancy (a single donor) has a low formation energy under *p*-type and semiinsulating conditions, and the Ga vacancy (a triple acceptor) gets a low formation energy under *n*-type conditions. Thus, based on the assumption of thermodynamic equilibrium, the dominant native defects are the vacancies: in *p*-type GaN the N vacancy, in *n*-type GaN the Ga vacancy.

The fact that the N vacancy (a donor) has a low formation energy under *p*-type conditions implies that it can be an efficient compensating center for acceptors. Similarly, under *n*-type conditions the Ga vacancy (an acceptor) has a low formation energy and can compensate donors. There is also strong evidence that the Ga vacancy or donor- V_{Ga} complexes are involved in the characteristic yellow luminescence observed in the photo-luminescence of GaN.¹¹

3.2 Hydrogen

Hydrogen is highly abundant in many of the high-temperature growth techniques such as MOCVD (metal-organic chemical vapor deposition) or HVPE (hydride vapor phase epitaxy). There is also strong experimental evidence that H is involved in the *p*-type doping of GaN.¹²

Let us briefly recall the properties of monatomic and molecular H in GaN.^{13,14} H exhibits a fundamental difference in behavior between *p*-type and *n*-type material. In *p*-type material H occupies the N-antibonding site, it behaves as a donor (it is positively charged), has a high solubility and a high diffusivity. In *n*-type conditions H is negatively charged (it is an acceptor) and a Ga-antibonding site is preferred. Compared to *p*-type conditions the diffusivity and solubility are dramatically reduced. Hydrogen is therefore an important

compensating center under *p*-type conditions. Under *n*-type conditions it is inefficient as a compensating center due to the low solubility.

4 *p*-type doping in GaN

4.1 Solubility

The solubility of dopants in GaN is limited by the formation of dopant clusters or the formation of chemical compounds between the acceptor species and N or Ga atoms. Our calculations show that the solubility of Mg is limited by the formation of Mg_3N_2 ; the reason is the high chemical stability of this compound (formation enthalpy: $\Delta H_f = 4.8 \text{ eV}$). For Ca the solubility is limited by Ca_3N_2 ($\Delta H_f = 4.6 \text{ eV}$). For Zn acceptors the solubility is limited by two phases: under Ga-rich conditions by bulk Zn, under N-rich conditions by Zn_3N_2 . The origin is the very low formation enthalpy of Zn_3N_2 ($\Delta H_f = 0.2 \text{ eV}$) which implies that this phase can be formed only under N-rich conditions.

For the following discussion we will fix the chemical potentials. For the Ga chemical potential we assume Ga-rich conditions (which appear to be common in experimental growth conditions). For the acceptors we set the chemical potential to its upper limit (we are interested in the maximum achievable acceptor concentration) which is given by their solubility limit. Using the same arguments we set the H chemical potential to that of H_2 molecules. Using these values for the chemical potentials the formation energy is solely a function of the Fermi energy.

4.2 Compensation

Before discussing the role of H in *p*-type doping let us briefly focus on the H-free case, i.e., only the acceptor and native defects are present. Figure 1 shows the corresponding formation energies as a function of the Fermi energy. As pointed out in Sec. 3.1 the dominant native defect under *p*-type conditions is the N vacancy; all other defects are higher in energy and outside the plot range. The slope of the formation energies characterizes the charge state; e.g., a positive slope (as found for the N vacancy) indicates a positive charge state, corresponding to a donor.

Using the calculated formation energies, and taking into account that the Fermi energy is fixed by the condition of charge neutrality, the equilibrium concentration [Eq. (1)] for each defect can be calculated as a function of temperature. At temperatures exceeding 1000 K the N vacancies increasingly compensate the acceptors.¹⁴ Lower-temperature growth techniques such as MBE (molecular beam epitaxy) should suffer less from this problem. This conclusion

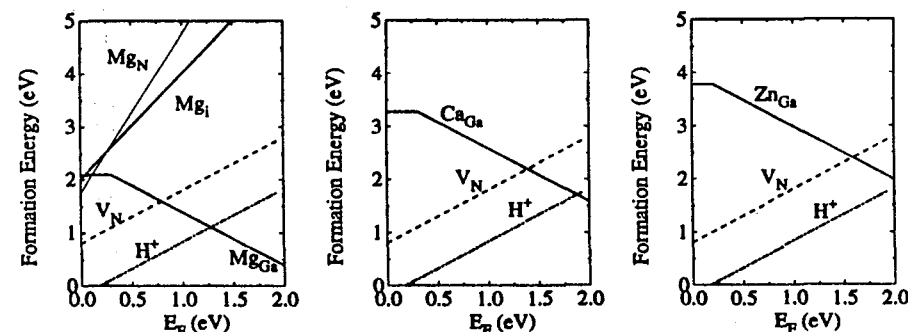


Figure 1: Formation energy as a function of the Fermi level for (a) Mg, (b) Ca, and (c) Zn in different configurations (Ga-substitutional, N-substitutional, and interstitial configuration). Also included are the native defects and interstitial H.

is consistent with the fact that only in MBE-grown GaN can *p*-type conductivity be achieved without any post-growth processing.^{15,16}

4.3 Role of H in achieving *p*-type doping

H-rich conditions are characteristic for many of the high-temperature growth techniques such as MOCVD and HVPE. Figure 1 shows that under these conditions H becomes the dominant donor; the formation energy of H is in the considered interval of Fermi energies always lower than the dominant native defect, the N vacancy. Since the acceptors and the hydrogen atoms are the dominant species, and since they carry opposite charge, charge neutrality requires that their equilibrium concentrations are equal for all temperatures, indicating that H is a very efficient compensating center. Further, compared to the H-free case the concentration of acceptors is *increased* and the defect concentration is *decreased*. Both effects are observed for all three acceptors (Mg, Ca, Zn) and are crucial to increase doping levels.

What is the mechanism by which H changes the acceptor and defect concentration? In a plot such as Fig. 1, the Fermi level position can be roughly estimated to be near the crossing point between the acceptor and the dominant donor species. At this point their formation energies (and hence their concentrations) are equal, ensuring charge neutrality.¹⁷ By going from H-free conditions to H-rich conditions the crossing point shifts to higher Fermi energies. An increase in the Fermi energy *generally* decreases the formation energy of acceptors and increases the formation energy of donors (defects), thus resulting in a lowered defect concentration and an increased acceptor concentration. We note that this mechanism works only if H is able to significantly shift the

Fermi energy which is the case if (i) H is the dominant donor (i.e., its formation energy must be lower than that of all native defects) and (ii) its formation energy must be comparable to that of the dopant impurity (a crossing point must exist in the band gap) which is the case for all three acceptors considered here.

Growing under H-rich conditions thus improves acceptor and defect concentrations, the downside being that the acceptors are almost completely compensated by the H impurities. Therefore, growing under H-rich conditions results in semiinsulating material, consistent with experimental observations.¹² In order to activate the acceptors, post-growth treatments are necessary to eliminate the compensation by H.

For Mg dopants the H donors and Mg acceptors can actually form electrically neutral complexes with a binding energy of ≈ 0.7 eV.¹³ Since the complex is mainly characterized by a strong N-H bond¹³ we expect similar complexes also for Zn and Ca acceptors. For the specific choice of chemical potentials made here, this binding energy is low enough for the complexes to be dissociated at the growth temperature; however, the Mg and H will form pairs when the sample is cooled to room temperature, consistent with experimental observations.¹⁸

The first step in the activation process is the dissociation of the H-acceptor complex. Our estimated dissociation barrier for the Mg-H complex is 1.5 eV, calculated by considering a jump to a nearest-neighbor site; the total barrier may be slightly higher.¹³ This barrier should be low enough to be overcome at modest annealing temperatures (around 300°C). Experimental results show, however, that activation has to be carried out at much higher temperatures ($> 600^\circ\text{C}$).¹² The reason is that dissociation alone is insufficient; in order to prevent the H from compensating the Mg acceptor it has to be either removed (to the surface or into the substrate) or neutralized (e.g., at an extended defect).

The calculated diffusion barrier for H^+ in GaN is low (≈ 0.7 eV¹³) indicating that H^+ is highly mobile and can easily migrate to the surface or extended defects. The high temperature necessary to activate the Mg and Ca acceptors therefore reflects an activation barrier for eliminating H as compensating center by incorporating it at extended defects (which typically occur in high concentrations in GaN¹⁹) or by removal of H through desorption at surfaces.

4.4 Incorporation on other sites

Another mechanism that may limit the hole concentration, is self-compensation of the acceptors: instead of being incorporated on the Ga substitutional site

the acceptor may be built in on other sites where it is electrically inactive or even becomes a donor. As possible configurations we have investigated the N substitutional site and several interstitial configurations. For all three acceptors considered here the behavior is very similar. We will therefore focus our discussion on Mg.

The calculated formation energies are displayed in Fig. 1. The positive slope in the formation energy indicates that Mg in both configurations acts as a donor: Mg_i as a double donor, Mg_N as a triple donor. Whereas the behavior of Mg_i is expected, the donor character for Mg_N is not as obvious: at first sight Mg should act as a triple acceptor. The replacement of the "small" N atom ($r_\text{cov} = 0.75 \text{ \AA}$) with a "large" Mg atom ($r_\text{cov} = 1.36 \text{ \AA}$) results in a large increase of the nearest neighbor bond length (by 24% !), giving rise to substantial changes in the positions of the defect levels. The large strain around the Mg atom further explains the high formation energy, rendering this site energetically unfavorable. We therefore conclude that Mg (and also Zn and Ca) will always prefer the Ga substitutional site: incorporation on other sites can be ruled out. For other possible acceptors (particularly elements with a small ionic radius), the situation may be different.

5 Conclusions

Based on first-principles calculations we have studied several mechanisms which may limit the hole concentration in GaN doped with Mg, Ca, and Zn. Two mechanisms are found to be important: (i) solubility issues (the formation of Mg_3N_2 , Ca_3N_2 , Zn_3N_2 , and bulk Zn) and (ii) the compensation by native defects. Incorporation of Mg, Zn, and Ca acceptors on the N site or in an interstitial configuration was found to be negligible. Combining our numerical results about native defects, interstitial H and acceptor impurities we could identify why H incorporation increases the acceptor concentration and simultaneously reduces compensation by native defects.

Acknowledgments

This work was supported in part by the DAAD (German Academic Exchange Service) and by ARPA under agreement no. MDA972-95-3-0008.

References

1. S. Nakamura, T. Mukai, and M. Senoh, *Appl. Phys. Lett.* **64**, 1687 (1994).

2. I. Akasaki, H. Amano, M. Kito, and K. Hiramatsu, *J. Lumin.* **48&49**, 666 (1991).
3. S. Fischer, C. Wetzel, E. E. Haller, and B. K. Meyer, *Appl. Phys. Lett.* **67**, 1298 (1995).
4. J. W. Lee, S. J. Pearton, J. C. Zolper, and R. A. Stall, *Appl. Phys. Lett.* **68**, 2102 (1996).
5. H. Morkoc, S. Strite, G. B. Gao, M. E. Lin, B. Sverdlov, and M. Burns, *J. Appl. Phys.* **76**, 1363 (1994).
6. G.-X. Qian, R. M. Martin, and D. J. Chadi, *Phys. Rev. B* **38**, 7649 (1992).
7. N. Troullier and J. L. Martins, *Phys. Rev. B* **43**, 1993 (1991).
8. J. Neugebauer and C. G. Van de Walle, *Phys. Rev. B* **50**, 8067 (1994).
9. R. Stumpf and M. Scheffler, *Comp. Phys. Commun.* **79**, 447 (1994).
10. J. Neugebauer and C. G. Van de Walle, *Proc. Mater. Res. Soc. Symp.* **408**, 43 (1995).
11. J. Neugebauer and C. G. Van de Walle, *Appl. Phys. Lett.* **68**, (1996).
12. S. Nakamura, N. Iwasa, M. Senoh, and T. Mukai, *Jpn. J. Appl. Phys.* **31**, 1258 (1992).
13. J. Neugebauer and C. G. Van de Walle, *Phys. Rev. Lett.* **75**, 4452 (1995).
14. J. Neugebauer and C. G. Van de Walle, *Appl. Phys. Lett.* **68**, 1829 (1996).
15. R. J. Molnar, T. Lei, and T. D. Moustakas, *Proc. Mater. Res. Soc. Symp.* **281**, 753 (1993).
16. M. E. Lin, C. Xue, G. L. Zhou, J. E. Greene, and H. Morkoc, *Appl. Phys. Lett.* **63**, 932 (1993).
17. Strictly speaking, this assumption is valid only if we ignore free carriers, a reasonable approximation if the Fermi level is far enough from the valence-band edge.
18. W. Götz, N. Johnson, J. Walker, D. P. Bour, H. Amano, and I. Akasaki, *Appl. Phys. Lett.* **67**, 2666 (1995).
19. S. D. Lester, F. A. Ponce, M. G. Craford, and D. A. Steigerwald, *Appl. Phys. Lett.* **66**, 1249 (1994).