

EFFECTS OF STOICHIOMETRY ON POINT DEFECTS AND IMPURITIES IN GALLIUM NITRIDE

C. G. VAN DE WALLE AND J. E. NORTHRUP

*Palo Alto Research Center, 3333 Coyote Hill Road, Palo Alto, CA 94304, USA
E-mail: vandewalle@parc.com*

J. NEUGEBAUER

*Fritz-Haber-Institut der Max-Planck-Gesellschaft,
Faradayweg 4-6, D-14 195 Berlin-Dahlem, Germany*

First-principles calculations of formation energies of point defects are used to evaluate deviations from stoichiometry in GaAs and GaN. A comparison shows that such deviations are much smaller in GaN than in GaAs. The physical reasons for this difference include the large size mismatch between Ga and N atoms, which renders interstitial and antisite defects unfavorable, and the high binding energy of N_2 molecules, which leads GaN to always deviate towards the Ga-rich side.

1 Introduction

Deviations from stoichiometry have long been considered to play a major role in GaN. Much of the early discussions centered on the perceived difficulty to incorporate nitrogen during the growth, which was thought to result in large concentrations of nitrogen vacancies (V_N) that would cause *n*-type doping. We now know that unintentional *n*-type doping is due to impurities such as oxygen, rather than V_N , and that Ga vacancies (V_{Ga}) are *more* likely to form than V_N under *n*-type conditions [1]. Gallium vacancies have been recognized to be the source of the yellow luminescence in GaN [2], while V_N (which are compensating centers in *p*-type GaN) give rise to blue luminescence [3].

A great deal of insight has been gained by calculating formation energies of all of the important point defects based on first-principles calculations. In this paper we use the previously computed formation energies for point defects in GaN to calculate deviations from stoichiometry as a function of temperature. For comparison, we also examine the deviation from stoichiometry in GaAs, based on first-principles formation energies [4]. For typical growth conditions, the deviations from stoichiometry in GaN are far smaller than what is observed in GaAs. The physical reason behind this difference will be addressed.

In Sec. 2 we briefly review the computational approach. Section 3 contains results for GaAs, while Sec. 4 addresses GaN. Section 5 summarizes and discusses our conclusions.

2 Computational approach

The equilibrium concentration of a defect in a semiconductor is given by

$$c = N_{\text{sites}} \exp(-G^f / kT) \quad (1)$$

where G^f is the Gibbs free energy of formation, and N_{sites} is the number of sites the defect can be incorporated on. For instance, for V_N in GaN N_{sites} is equal to the number of nitrogen sites in the crystal ($\sim 4.4 \times 10^{22} \text{ cm}^{-3}$). k is the Boltzmann constant, and T the temperature. Equation (1) shows that defects with a high formation energy will occur in low concentrations.

The Gibbs free energy can be written as $G = E - TS + pV$. The pressure-volume term is typically negligible, but the entropy term may be sizeable at high temperatures. First-principles calculations of vibrational entropies are feasible but time-consuming; values in the range of 1 to 10 k are typical for many point defects. In the following we assume an entropy of 5 k for all defects.

The formation energy of a V_N in charge state +1 is expressed as

$$E^f(V_N^+) = E^{\text{tot}}(V_N^+) - E^{\text{tot}}(\text{bulk}) + \mu_N + E_F \quad (2)$$

where $E^{\text{tot}}(V_N^+)$ is the total energy of the defect, calculated in a first-principles supercell calculations, and $E^{\text{tot}}(\text{bulk})$ is the energy of a similar supercell containing the perfect crystal. μ_N is the chemical potential of nitrogen. Nitrogen-rich conditions correspond to μ_N being equal to the energy of an N_2 molecule; gallium-rich conditions correspond to μ_{Ga} equal to the energy of bulk Ga. In equilibrium, $\mu_{\text{Ga}} + \mu_N = \mu_{\text{GaN}}$; the range of the chemical potentials thus corresponds to the heat of formation of GaN.

E_F is the Fermi energy, which is determined by the condition of charge neutrality. Expressions like Eq. (2) can be written for each of the point defects in the system, in each of their possible charge states. The Fermi level then has to be adjusted so as to yield concentrations for each of these defects that produce a net charge of zero in the system (including contributions from free carriers). This amounts to solving a polynomial equation in $\exp(-E_F/kT)$. We have not included effects of temperature on the band-edge positions, but have checked that our qualitative conclusions would remain unaffected.

The first-principles calculations from which we derive the energies needed in Eq. (2) are based on density-functional theory within the local density approximation (LDA) and the pseudopotential-plane-wave method. Details of these calculations can be found in Refs. [1] and [4].

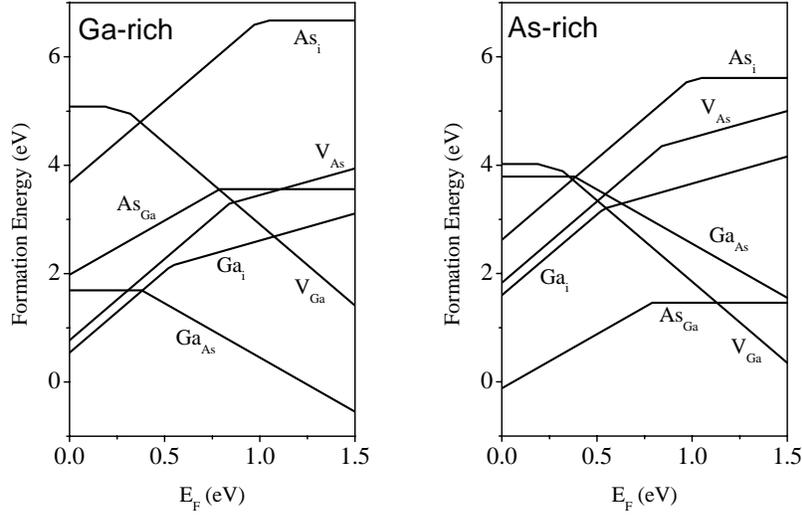


Fig. 1: First-principles formation energies (from Ref. [4]) as a function of Fermi level for native point defects in GaAs, for Ga-rich and As-rich conditions. $E_F=0$ corresponds to the valence-band maximum.

3 Results for GaAs

First-principles formation energies for all native point defects in GaAs, as reported in Ref. [4], are shown in Fig. 1. These values are in reasonable agreement with the results of more recent calculations, e.g., in Ref. [5]. We have used these energies to evaluate the deviation from stoichiometry as a function of temperature, under Ga-rich and As-rich conditions. The temperature dependence of the bounds on the chemical potential was not taken into account. The results are shown in Fig. 2. The deviation from stoichiometry is defined as

$$\delta = \Sigma[\text{As}_i] - \Sigma[\text{Ga}_i] - \Sigma[\text{V}_{\text{As}}] + \Sigma[\text{V}_{\text{Ga}}] + 2 \Sigma[\text{As}_{\text{Ga}}] - 2 \Sigma[\text{Ga}_{\text{As}}]$$

with the sums running over all possible charge states. Positive values of δ thus correspond to an excess of arsenic.

Employing the calculated formation energies we find that for $\mu_{\text{As}} = \mu_{\text{As}(\text{bulk})}$ there is an excess of As in the crystal, and for $\mu_{\text{Ga}} = \mu_{\text{Ga}(\text{bulk})}$ there is an excess of Ga. This result may seem obvious, but it is actually nontrivial, as we will see in

the next section when discussing GaN. The result also agrees with experiment [6].

On the As-rich side, the computed values reported in Fig. 2 are in reasonable agreement with experimental values for deviations from stoichiometry in melt-grown, as analyzed and reported in a review paper by Hurlé [6]. On the Ga-rich side, however, the analysis of Ref. [6] shows a much larger deviation δ at temperatures as low as 600 K. This discrepancy cannot be attributed to an error in the computed formation energies for Ga-rich defects, because the mere presence of a defect with lower formation energy could not explain the shape of the curve reported by Hurlé (Fig. 45 in Ref. [6]). We speculate that the discrepancy may be due to the presence of unintentional contaminants in the crystals. For instance, the presence of carbon would, under Ga-rich conditions, lead to incorporation of C_{As} , which is an acceptor. The resulting p -type conditions would, in turn, favor incorporation of Ga_i (see Fig. 1).

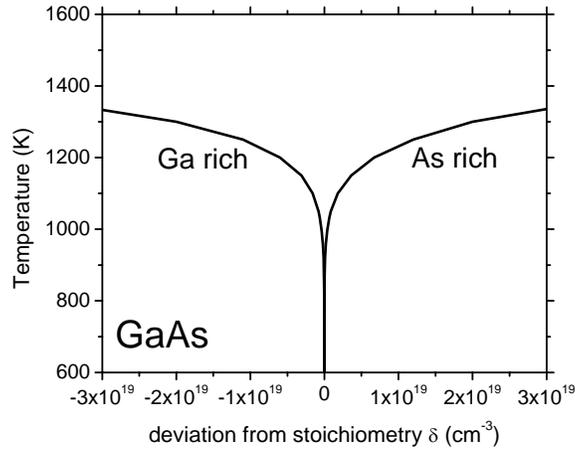


Fig. 2: Calculated deviation from stoichiometry under equilibrium conditions, based on the first-principles formation energies shown in Fig. 1. Positive values of δ correspond to an excess of arsenic.

4 Results for GaN

Figure 3 shows first-principles formation energies for all native point defects in GaN. The values are largely the same as were reported in Ref. [1], but have been updated with more recent calculations carried out in 96-atom wurtzite supercells. These energies were used in the evaluation of the deviation from stoichiometry as a function of temperature, under Ga-rich and N-rich conditions, as reported in Fig. 4.

One immediately notices that the deviations from stoichiometry for GaN are much smaller than in the case of GaAs. To some extent, this is due to our choice of temperature range for the plots in Fig. 2. Indeed, if one plots δ as a function of T/T_m , where T_m is the melting temperature (1511 K for GaAs and 2791 K for GaN), the curves for GaAs and GaN look a lot more similar. However, the range of temperatures in Figs. 2 and 4 was actually chosen to be representative of conditions typically used for growth of these materials. As can be seen in Figs. 2 and 4, deviations from stoichiometry become larger than 2×10^{17}

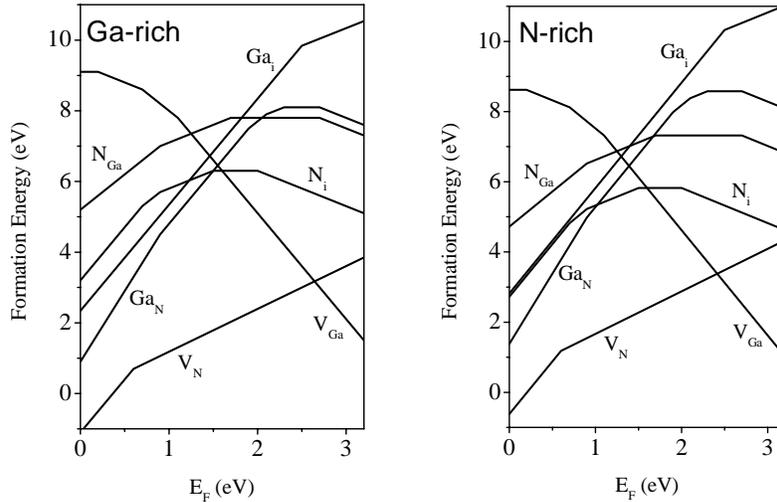


Fig. 3: First-principles formation energies as a function of Fermi level for native point defects in GaN, for Ga-rich and N-rich conditions. $E_F=0$ corresponds to the valence-band maximum.

cm^{-3} when $T \approx 2/3 T_m$. In the case of GaAs, such conditions are routinely achieved during growth, but in the case of GaN, such temperatures would require a very high nitrogen overpressure, and are approached only in the case of high-pressure bulk crystal growth [7].

One could argue that the relatively lower growth temperatures used for GaN are more likely to lead to nonequilibrium conditions that could lead to incorporation of point defects beyond the equilibrium concentrations shown in Fig. 4. However, such deviations from equilibrium concentrations can only be achieved if the diffusivities of point defects are sufficiently low. Our investigations of point-defect migration [8] show that migration barriers for point defects in GaN are quite modest, and not higher than they are in GaAs, indicating that kinetically induced deviations from equilibrium would be difficult to achieve.

A second feature of the plot for GaN in Fig. 4 is that, even under N-rich conditions, the deviation from stoichiometry is towards the Ga-rich side (i.e., $\delta < 0$). The reason for this unusual behavior is that, even under N-rich conditions, the nitrogen vacancy remains the dominant defect in GaN (see Fig. 3). Under both Ga-rich and N-rich conditions, equilibrium defect concentrations are dominated by V_N , acting as a donor. However, it should be clear that the n -type doping due to V_N results in very low electron concentrations.

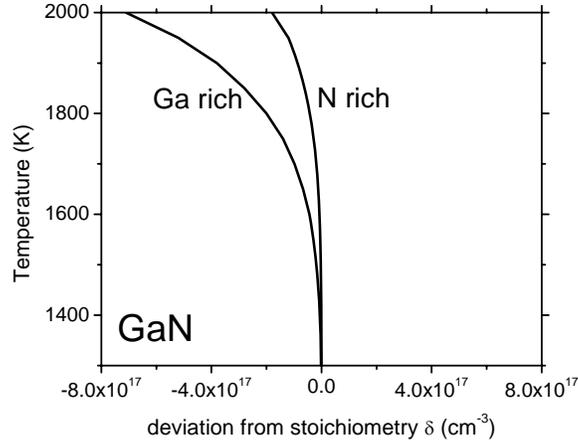


Fig. 4: Calculated deviation from stoichiometry under equilibrium conditions, based on the first-principles formation energies shown in Fig. 3. Positive values of δ correspond to an excess of nitrogen.

We point out that larger deviations from stoichiometry may occur in the presence of extrinsic impurities; indeed, doping shifts the Fermi level towards the band edges, resulting in lower formation energies for specific point defects. We also note that deviations from stoichiometry could occur in heavily dislocated material due to the presence of non-stoichiometric dislocation cores. As an example consider a dislocation density of $5 \times 10^9 \text{ cm}^{-2}$ and suppose that along the core there are six extra Ga atoms every 5 \AA , as in the case of the (6:0) model [9] for screw dislocations in Ga-rich GaN. In this case the deviation from stoichiometry arising from the dislocations is $6 \times 10^{17} \text{ cm}^{-3}$. This would not be significant compared to the contribution from point defects in the case of GaAs. However, in GaN the contribution from the dislocations might become relevant when the dislocation density exceeds 10^9 cm^{-2} .

5 Summary and discussion

We have calculated deviations from stoichiometry based on first-principles formation energies for GaAs and GaN. We focused on deviations from stoichiometry due to point defects in the absence of extrinsic impurities. The values for GaAs are in line with expectations based on experimental observations, although some discrepancy on the Ga-rich side may merit further investigation. The deviations from stoichiometry are much smaller in the case of GaN, and are exclusively due to formation of nitrogen vacancies.

The difference between GaAs and GaN can be attributed to the fact that in GaN, only vacancies have low enough formation energies to ever occur in sizeable concentrations, whereas in GaAs interstitials and antisites are competitive with vacancies. The physical reason for this difference lies in the large difference between the chemical constituents of GaN: Ga and N have very different atomic sizes, which results in high formation energies for interstitial and antisite defects – unlike the case of GaAs, where Ga and As have comparable sizes.

In addition, the high binding energy of nitrogen molecules makes it difficult (or even impossible) for the GaN solid to become nitrogen-rich: nitrogen atoms much prefer to leave the solid and become part of N_2 molecules, rather than incorporate in the solid in the form of nitrogen-rich point defects. Again, this feature is absent in the case of GaAs, where As molecules exhibit only modest binding energies.

Based on these considerations and on our calculated values, we conclude that point-defect induced deviations from stoichiometry are expected to be far less important in GaN than they are in GaAs or other III-V compounds.

Acknowledgments

This work was supported by the Air Force Office of Scientific Research, Contract No. F4920-00-C-0019, monitored by G. Witt. J. N. thanks the Deutsche Forschungsgemeinschaft "SFB 296".

References

- [1] J. Neugebauer and C. G. Van de Walle, "Atomic geometry and electronic structure of native defects in GaN", *Phys. Rev. B* **50**, 8067 (1994)
- [2] J. Neugebauer and C. G. Van de Walle, "Gallium vacancies and the yellow luminescence in GaN", *Appl. Phys. Lett.* **69**, 503 (1996)
- [3] C. G. Van de Walle, "Interactions of hydrogen with native defects in GaN", *Phys. Rev. B* **56**, 10 020 (1997)
- [4] J. E. Northrup and S. B. Zhang, "Dopant and defect energetics: Si in GaAs", *Phys. Rev. B* **47**, 6791 (1993); "Energetics of the As vacancy in GaAs: The stability of the 3+ charge state", *Phys. Rev. B* **50**, 4962 (1994)
- [5] J. T. Schick, C. G. Morgan, and P. Papoulias, "First-principles study of As interstitials in GaAs: Convergence, relaxation, and formation energy", *Phys Rev. B (in press)*
- [6] D. T. J. Hurle, "A comprehensive thermodynamic analysis of native point defect and dopant solubilities in gallium arsenide", *J. Appl. Phys.* **85**, 6957 (1999)
- [7] S. Porowski, "Bulk and homoepitaxial GaN – growth and characterization", *J. Cryst. Growth* **189/190**, 153 (1998)
- [8] S. Limpijumnong and C. G. Van de Walle (*unpublished*)
- [9] J. E. Northrup, "Theory of intrinsic and H-passivated screw dislocations in GaN", *Phys. Rev. B* **66**, 045204 (2002)