Deep acceptors trapped at threading edge dislocations in GaN

J. Elsner[1,2], R. Jones[1], M. Haugk[2], Th. Frauenheim[2], M.I. Heggie[3], S. Öberg[4], P. R. Briddon[5]

[1] *Department of Physics, University of Exeter, Exeter, EX4 4QL, UK*

[2] *Technische Universität, Theoretische Physik III, D - 09107 Chemnitz, Germany*

[3] *CPES, University of Sussex, Falmer, Brighton, BN1 9QJ, UK*

[4] *Department of Mathematics, University of Luleå, Luleå, S97 187, Sweden*

[5] *Department of Physics, University of Newcastle upon Tyne, Newcastle, NE1 7RU, UK*

Abstract

Local density functional methods are used to examine the behavior of the gallium vacancy, oxygen and related defect complexes trapped at threading edge dislocations in GaN. These defects are found to be particularly stable at the core of the dislocation where oxygen sits two–fold coordinated in a bridge position. V_{Ga}–O_N is found to be a deep double accecptor, V_{Ga}–$(O_N)_2$ is a deep single acceptor and V_{Ga}–$(O_N)_3$ at the dislocation core is inactive. We suggest that the first two defects are responsible for a deep acceptor level associated with the mid-gap yellow luminescence band.

GaN has recently gained a considerable interest due to its optoelectronic materials properties, characterised by its wide band gap (3.4 eV for wurtzite GaN) which enables applications demanding blue light. Defect–induced electronic states in the band gap can significantly alter the optical performance. This fact becomes extremely important in laser devices, where parasitic components in the emission spectrum are highly undesirable. The most commonly observed emission in n–type GaN, the yellow luminescence (YL), is centered at 2.2-2.3 eV with a line width of $\approx$ 1 eV. Several models for the origin of the YL in GaN have been proposed. Most assume the transition is between a shallow donor and a deep acceptor [**?**] or a deep donor and a shallow acceptor [**?**]. Recent work has however found evidence for the deep acceptor model [1]. Cathodoluminescence (CL) studies have shown that the YL is spatially non-uniform but can be correlated with extended defects and especially low angle grain boundaries containing dislocations [2]. Furthermore, atomic force microscopy in combination with CL has led to the conclusion that threading dislocations act as non-radiative recombination centres and degrade the luminescence efficiency in the blue light spectrum of the epilayers [3].

Threading edge dislocations, parallel to **c** with Burgers vectors **a** and densities $\sim 10^9$ cm^{-2} persist beyond $\sim 0.5\mu$m above the interface [4–6] of wurtzite GaN samples grown by metal–organic chemical vapor deposition (MOCVD) or molecular beam epitaxy (MBE). They thus cross the active region of the devices and could contribute to the YL. In a previous letter [7] we presented the atomic geometry for the threading edge dislocation which has recently been confirmed by atomic resolution Z–contrast imaging [8]. However, we found that in the defect free form the threading edge dislocation has a band free from deep gap states and the pure dislocation could not be responsible for the yellow luminescence [7].

Gallium vacancies (V_{Ga}) were detected by positron annihilation studies in bulk GaN and their concentration was found to be related to the intensity of the YL [9]. The relevant transition level in n–type GaN is at the center of the YL spectrum ($E^{2-/3-} \approx 1.1$ eV referenced to the top of the valence band [10]). As a triple acceptor the gallium vacancy is three–fold negatively charged in n–type GaN and can attract up to three positively charged donors. Recent experimental [11–13] and theoretical [14] work suggest that oxygen ot a nitrogen site (O_N) is the main cause of unintentional n-type conductivity in GaN. V_{Ga} forms defect complexes with O_N which sits as a next neighbour of V_{Ga} to reduces the Coulomb energy [10,15]. V_{Ga} related defect complexes in GaN were found to have electrical properties dominated by the Ga vacancy [10], i.e. they are acceptors and exhibit gap states above the top of the valence band arising from the N dangling bonds surrounding V_{Ga}. Furthermore, Youngman and Harris [16] studied the violet luminescence (VL) in AlN, which is believed to have essentially the same origin as the YL in GaN [15]. They found the VL in AlN to be correlated with the oxygen incorporation and extended defects which are also known to contain substantial amounts of oxygen [17]. Hence, in analogy to the VL in AlN it has been suggested that the YL in n–type GaN is caused by O related defect complexes.

In this letter we explore the energetics and geometries of the Ga vacancy, oxygen and related gallium vacancy–oxygen defect complexes V_{Ga}–$(O_N)_n$ ($n = 1, 2, 3$) in the stress field of threading edge dislocations in GaN using an *ab initio* local density functional (LDF) cluster method, *AIMPRO*, and a charge self–consistent density functional based tight binding method *SCC–DFTB* which we apply to supercells in order to obtain formation energies. For a description of the *AIMPRO* and *SCC–DFTB* methods and applications to GaN see references [18,19,7] and references [20,7,21,22] respectively.

As an illustrative benchmark for the application of the *SCC–DFTB* method to O in GaN we choose the $(V_{Ga}–O_N)^{2-}$ defect complex (see Fig. 1) as well as its constituents, V_{Ga}^{3-} and O_N^+. These defects have previously been investigated by Neugebauer *et al.* [10,23] and Mattila *et al.* [15] using plane wave SCF–LDA methods. In this work the defects are modeled in a 128 atom wurtzite supercell using two k-points to sample the Brillouin zone. As in ref. [10,23,15] formation energies are evaluated assuming Ga–rich growth conditions, which are common in many growth techniques, O in equilibrium with Ga_2O_3, corresponding to an upper limit for the O concentration [23], and n–type material, i.e. the Fermi level is pinned close to the conduction band minimum. The atomic geometry of the triply charged Ga vacancy is characterised by a strong outward relaxation of the surrounding N atoms. The three equivalent N atoms relax by 10.2% (11.8% in ref. [10]) outwards and the remaining N atom moves 9.5% in [0001] (10.6% in ref. [10]). The formation energy is low (1.6 eV in this work, ≈ 1.3 eV in ref. [10] and ≈ 1.5 eV in ref. [15]). Oxygen on a nitrogen site has slightly larger Ga–O bonds than the Ga–N bond length in bulk GaN (1.95 Å). We obtain again a low formation energy of 1.7 eV (≈ 1.7 eV in ref. [10] and ≈ 1.6 eV in ref. [15]). Bringing V_{Ga}^{3-} and O_N^+ together one gets $(V_{Ga}–O_N)^{2-}$. We find the distance between the vacancy core and the O (N) increased by 13.5% (8.9%) which is in good agreement with the values of 14.9% (9.8%) given by Neugebauer *et al.* [10]. Furthermore, we determined the energy ΔE

for the reaction,

$$(V_{\rm Ga} - O_{\rm N})^{2-} \rightarrow V_{\rm Ga}^{3-} + O_{\rm N}^{+},$$

to be 2.2 eV in good agreement with the plane wave methods (1.8 eV in ref. [10] and $\approx$ 2.1 eV in ref. [15]). We thus get an absolute formation energy of $\sim$ 1.1 eV which is again very close to the plane wave values ($\sim$ 1.1 eV in ref. [10] and $\sim$ 0.9 eV in ref. [15]) suggesting a high equilibrium concentration of $\sim 10^{18}/\mathrm{cm}^3$ [10,15] at a usual MOCVD growth temperature of $\sim$ 1300 K.

We now investigate $\mathrm{V}_{\rm Ga}^{3-}$, $\mathrm{O}_{\rm N}^{+}$ and $(\mathrm{V}_{\rm Ga}\text{–}(\mathrm{O}_{\rm N})_n)^{(3-n)-}$ $(n = 1, 2, 3)$ in the stress field of threading edge dislocations. In the *SCC–DFTB* case the dislocations are modeled in a 312 atom supercell containing a dislocation dipole (see Fig. 2). In the AIMPRO case, we used 286 atom stoichiometric clusters with one dislocation. In a previous work [7] we found the structure of the most stable dislocation to have a closed core (see Fig. 2) consisting of a pair of three–fold coordinated sp^2 (p^3) hybridised Ga (N) atoms arranged in a dimer as at the $(10\overline{1}0)$ surface [24]. In analogy to the $(10\overline{1}0)$ surface we found the threading edge dislocation to be electrically inactive. For a detailed discussion of the atomic geometry, electrical properties and the line energy see ref. [7].

Firstly we place the point defects into a bulk like position, i.e. a position with a very small stress field, far away from the dislocation core in the supercell (position 0 in Fig. 2). In order to reduce the interaction between the point defects we doubled the 312 atom supercell along the dislocation line, i.e. in [0001], to obtain a 624 atom supercell. At position 0 in this cell we find the atomic geometries and formation energies of the point defects to be in good agreement with the values obtained in the 128 atom perfect lattice supercell (see first two lines in Table I). We now put the defects at different positions (pos. 1,2,3 in Fig. 2) in the dislocation stress field. The resulting formation energies are summarised in Table I.

$\mathrm{V}_{\rm Ga}^{3-}$ is trapped in the dislocation stress field, in particular, at the dislocation core (pos. 1 in Fig. 2) and at pos. 2. Ga atoms in these positions would have high energies, caused by the under–coordination in pos. 1 or by the strongly strained bonds in pos. 2 (2.11 Å average bond length). This makes the formation of vacancies at these positions energetically favorable (see Table I). It should be noted that at position 1 a Ga vacancy creates a two–fold coordinated N atom which would result in a high energy. However, since Ga atoms at position 4 and 4* are quite close to the N atom at position 1, this N atom forms a bond (2.00 Å) with one of these Ga atoms and thus achieves three–fold coordination.

Oxygen atoms sit preferentially two or three–fold coordinated. This explains why $\mathrm{O}_{\rm N}^{+}$ is by 1.3 eV more stable at the dislocation core (pos. 1) where it replaces a three–fold coordinated N atom than in a bulk like region (pos. 0) where it is four–fold coordinated.

The high stabilities of $\mathrm{V}_{\rm Ga}^{3-}$ and $\mathrm{O}_{\rm N}^{+}$ at the dislocation core imply also a very low formation energy for $(\mathrm{V}_{\rm Ga}\text{–}\mathrm{O}_{\rm N})^{2-}$ (-3.3 eV below the energy for pos. 0) and hence a high concentration. Here O sits two–fold coordinated in a bridge position with very strong Ga–O bonds (1.72 Å). Due to these strong bonds and the high complex binding energy of 2.3 eV at the dislocation core we expect $(\mathrm{V}_{\rm Ga}\text{–}\mathrm{O}_{\rm N})^{2-}$ to be immobile. Finally, we investigated $(\mathrm{V}_{\rm Ga}\text{–}(\mathrm{O}_{\rm N})_2)^{-}$ and $\mathrm{V}_{\rm Ga}\text{–}(\mathrm{O}_{\rm N})_3$, which in analogy to $(\mathrm{V}_{\rm Ga}\text{–}\mathrm{O}_{\rm N})^{2-}$ are found to be particulary stable at the core of the threading edge dislocations where they are likely to be immobile. This suggests that $(\mathrm{V}_{\rm Ga}\text{–}(\mathrm{O}_{\rm N})_n)^{(3-n)-}$ $(n = 1, 2, 3)$ increase the oxygen concentration near to threading edge dislocations.

The calculations reveal that $(\mathrm{V}_{\rm Ga}\text{–}\mathrm{O}_{\rm N})^{2-}$ and $(\mathrm{V}_{\rm Ga}\text{–}(\mathrm{O}_{\rm N})_2)^{-}$ defects are deep double and single acceptors respectively (with gap states ~ 1.2 eV above VBM) and these defects might be associated with the yellow luminscence. V_{Ga}–$(O_N)_3$ has a deep gap state (~ 1.0 eV above VBM) which comes from a three–fold coordinated nitrogen atom in a bulk position. At the dislocation core (pos. 1), however, for V_{Ga}–$(O_N)_3$ all three–fold coordinated nitrogens surrounding the Ga vacancy are replaced by oxygen. At this position we find that V_{Ga}–$(O_N)_3$ is electrically inactive.

In conclusion, the density functional calculations show that in wurtzite GaN the stress field of threading edge dislocations is likely to trap gallium vacancies, oxygen and gallium vacancy–oxygen defect complexes. The most favorable position for gallium vacancy–oxygen complexes is at the dislocation core where oxygen sits two–fold coordinated with very strong Ga–O bonds and is therefore immobile. Following previous studies [10,15] we find that the gallium vacancy and oxygen related defect complexes are electrically active and suggest that they increase the intensity of the yellow luminescence near threading edge dislocations consistent with cathodoluminescence studies [2].

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TABLES

TABLE I. Formation energies in of V_{Ga}^{3-}, O_N^+, $(V_{Ga}\text{–}O_N)^{2-}$, $(V_{Ga}\text{–}(O_N)_2)^{1-}$ and $V_{Ga}\text{–}(O_N)_3$ in a 128 atom bulk cell and at the threading edge dislocation (see Fig. 2). Ga–rich growth conditions, O in equilibrium with Ga_2O_3 and n–type material are assumed.

position	$E(V_{Ga})$	$E(O_N^+)$	$E(V_{Ga}\text{–}O_N)^{2-}$	$E(V_{Ga}\text{–}O_{2N})^{-}$	$E(V_{Ga}\text{–}O_{3N})$
bulk cell	1.8	1.7	1.1	0.7	0.8
pos. 0 (bulk like)	1.7	1.5	1.0	0.9	0.7
pos. 1 (core)	-0.2	0.2	-2.3	-2.5	-3.0
pos. 2	-0.3	1.3	-0.6	-0.3	-0.3
pos. 3	0.3	1.0	-1.0	-1.0	-0.8

FIGURES

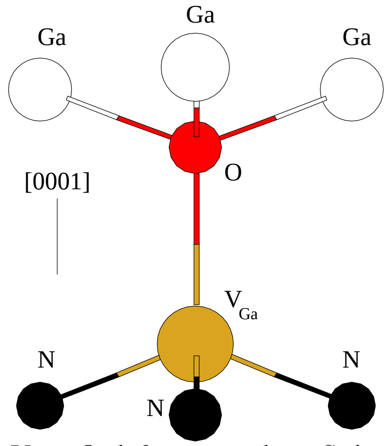

FIG. 1. Schematic view of the V_{Ga}–O defect complex. Substituting further three–fold coordinated N by O leads to V_{Ga}–$(O_N)_2$ and V_{Ga}–$(O_N)_3$.

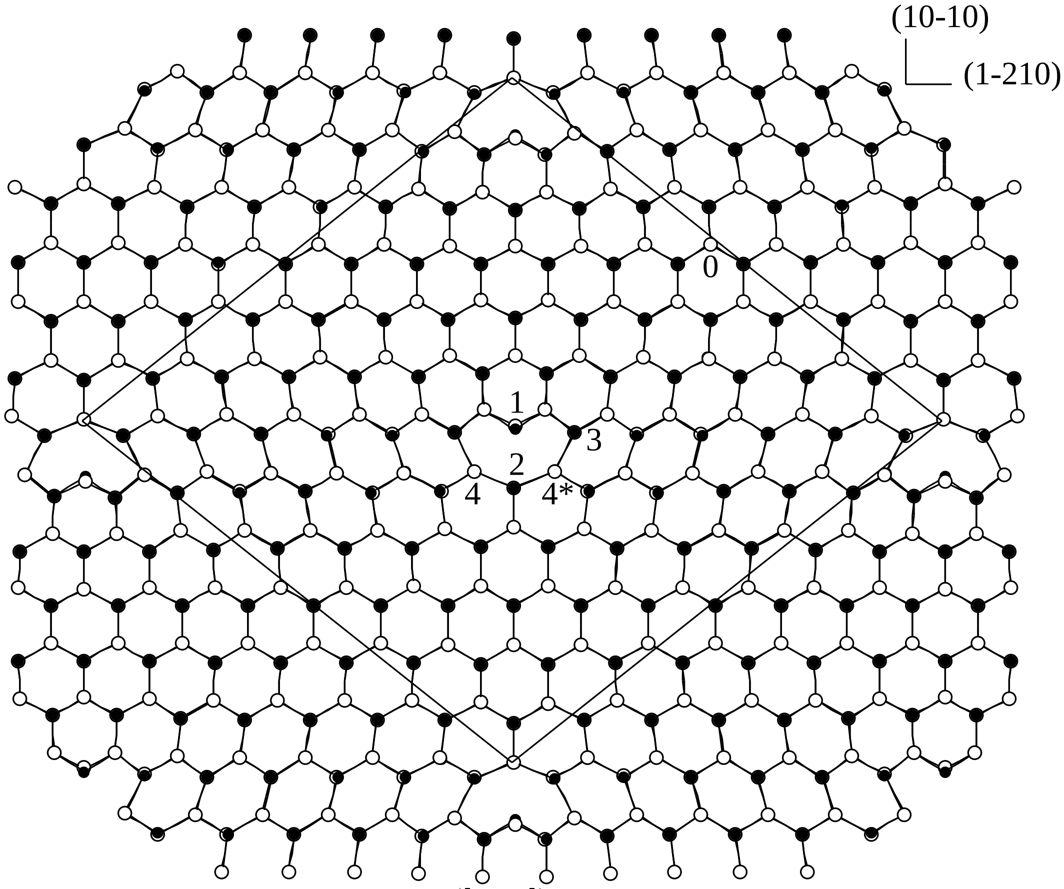

FIG. 2. View along the dislocation line ([0001]) of the 312 atom wurtzite supercell containing a dipole of threading edge dislocations with Burgers vector $b = [11\bar{2}0]$. White (black) circles represent Ga (N) atoms. Position 0 corresponds to a bulk like region. Position 1 is at the dislocation core which, similar to the GaN $(10\bar{1}0)$ surface, contains three–fold coordinated Ga (N) atoms in sp^2 (p^3) hybridisations. Positions 2 and 3 are situated in the stress field near to the dislocation core.

REFERENCES

[1] M. Godlewski *et al.*, Mat. Sci. Forum **258–263**, 1149 (1997).

[2] F. A. Ponce, D. B. Bour, W Gotz, and P. J. Wright, Appl. Phys. Lett. **68**, 57 (1996). Recent combined cathodoluminescence and atomic force microscopy points to threading dislocations as a source for these centers [3]

[3] S. J. Rosner, E. C. Carr, M. J. Ludowise, G. Girlami, and H. I. Erikson, Appl. Phys. Lett. **70**, 420 (1997).

[4] X. H. Wu, L. M. Brown, D. Kapolnek, S. Keller, B. Keller, S. P. DenBaars, and S. J. Speck, J. Appl. Phys. **80**, 3228 (1996).

[5] X.J. Ning, F.R. Chien, and P. Pirouz, J. Mater. Res. **11**, 580 (1996)

[6] F.A. Ponce, D. Cherns, W.T. Young, and J.W. Steeds, Appl. Phys. Lett. **69**, 770 (1996).

[7] J. Elsner, R. Jones, P.K. Sitch, V.D. Porezag, M. Elstner, Th. Frauenheim, M.I. Heggie, S. Öberg and P.R. Briddon, Phys. Rev. Lett. **79**, 3672 (1997).

[8] Y. Xin, S.J. Pennycook, N.D. Browning, P.D. Nelist, S. Sivananthan, J–P Faurie and P. Gibart, submitted to Appl. Phys. Lett. 1998.

[9] K. Saarinen *et al.*, Phys. Rev. Lett. **79** 3030 (1997).

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

[11] C. Wetzel *et al.*, Phys. Rev. Lett. **78**, 3923 (1997).

[12] C. Wetzel *et al.*, Proc. ICPS 23 (World Scientific, Singapore), 2929 (1996).

[13] P. Perlin *et al.*, Proc. Mater. Res. Soc. Symp. **449**, 519 (1997).

[14] C.G. Van de Walle and J. Neugebauer, Mater. Sci. Forum **258–263**, 19 (1997).

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

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

[17] A.D. Westwood *et al.*, J. Mater. Res. **10**, 1270 (1995).

[18] Jones, R.; *Phil. Trans. Roy. Soc. Lond. A* 1995, **350**, 189.

[19] Jones, R. and P.R. Briddon, in "The *ab initio* cluster method and the dynamics of defects in semiconductors", Semiconductors and Semimetals: Identification of Defects in Semiconductors, edited by M. Stavola (Academic Press: New York, 1997).

[20] D. Porezag, Th. Frauenheim and Th. Köhler Phys. Rev. B **51**, 12947 (1995).

[21] J. Elsner, M. Haugk, G. Jungnickel and Th. Frauenheim, Sol. State Comm. **106**, 739 (1998).

[22] M. Elstner, D. Porezag, G. Jungnickel, J. Elsner, M. Haugk, G. Jungnickel, Th. Frauenheim, S. Shuhai and G. Seifert, accepted for publication in Phys. Rev. B 1998 (code BJJ652B).

[23] J. Neugebauer, C.G. Van de Walle, Festkörperprobleme **35**, 25 (1996).

[24] J.E. Northrup, J. Neugebauer, Phys. Rev. B **53**, R10477 (1996).