Deep acceptors trapped at threading-edge dislocations in GaN

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Local-density-functional methods are used to examine the behavior of the oxygen defect, gallium vacancy, 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 twofold coordinated in a bridge position. V_{Ga}-$\mathrm{O_N}$ is found to be a deep double acceptor, V_{Ga}-$(\mathrm{O_N})_2$ is a deep single acceptor, and V_{Ga}-$(\mathrm{O_N})_3$ at the dislocation core is electrically inactive. We suggest that the first two defects are responsible for a deep acceptor level associated with the midgap yellow luminescence band. [S0163-1829(98)07143-4]

GaN has recently been the subject of considerable interest due to its optoelectronic properties. In particular the wide band gap (3.4 eV for wurtzite GaN) makes blue light applications feasible. 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 linewidth of $\approx$1 eV. Several models for the origin of the YL in GaN have been proposed. Most assume the transition to be between a shallow donor and a deep acceptor[1] or a deep donor and a shallow acceptor.[2] Recent work has, however, found evidence for the deep acceptor model.[3] Cathodoluminescence (CL) studies have shown that the YL is spatially nonuniform but can be correlated with extended defects and especially low angle grain boundaries containing dislocations.[4] Furthermore, atomic force microscopy in combination with CL has led to the conclusion that threading dislocations act as nonradiative recombination centers, and degrade the luminescence efficiency in the blue-light spectrum of the epilayers.[5]

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

Gallium vacancies (V_{Ga}) have been detected by positron annihilation studies in bulk GaN, and their concentration was found to be related to the intensity of the YL.[11] The relevant transition level in n-type GaN is at the center of the YL spectrum ($E^{2-/3-}$ referenced to the top of the valence band was calculated to be $\approx$1.1 eV in Ref. 12 and $\approx$1.5 eV in Ref. 17.) As a triple acceptor the gallium vacancy is threefold negatively charged in n-type GaN and can attract up to three positively charged donors. Recent experimental[13–15] and theoretical[16] work suggest that oxygen at a nitrogen site ($\mathrm{O_N}$) is the main cause of unintentional n-type conductivity in GaN. V_{Ga} forms defect complexes with $\mathrm{O_N}$ which sits as a next neighbor of V_{Ga} to reduce the Coulomb energy.[12,17] V_{Ga}-related defect complexes in GaN were found to have electrical properties dominated by the Ga vacancy,[12] 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[18] studied the violet luminescence (VL) in AlN, which is believed to have essentially the same origin as the YL in GaN.[17] They found the VL in AlN to be correlated with the oxygen incorporation

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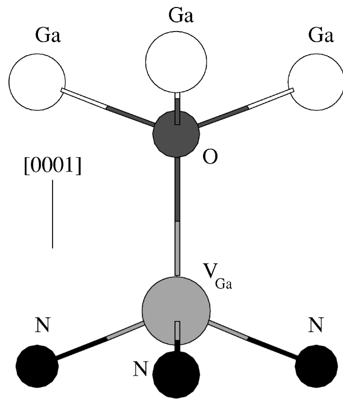
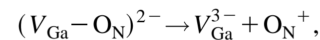


FIG. 1. Schematic view of the V_{Ga}-O defect complex. Substituting further threefold-coordinated N by O leads to V_{Ga}-$(\mathrm{O_N})_2$ and V_{Ga}-$(\mathrm{O_N})_3$.

and extended defects which are also known to contain substantial amounts of oxygen.[19] 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 paper we explore the energetics and geometries of the Ga vacancy, oxygen, and related gallium vacancy-oxygen defect complexes V_{Ga}-$(\mathrm{O_N})_n$ ($n=1, 2$, and 3) in the stress field of threading edge dislocations in GaN using an *ab initio* local-density-functional cluster method AIMPRO, and a self-consistent charge 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 Refs. 20, 21, and 9 and Refs. 22, 9, 23, and 24, respectively.

As an illustrative benchmark for the application of the SCC-DFTB method to O in GaN, we choose the $(V_{\mathrm{Ga}}\text{-}\mathrm{O_N})^{2-}$ defect complex (see Fig. 1), as well as its constituents, V_{Ga}^{3-} and $\mathrm{O_N}^{+}$. These defects were previously investigated by Neugebauer and Van de Walle[12,25] and Mattila and Nieminen[17] using plane-wave self-consistent field local-density-approximation 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. 12, 25, and 17, formation energies are evaluated assuming Ga-rich growth conditions, which are common in many growth techniques, O in equilibrium with $\mathrm{Ga_2O_3}$, corresponding to an upper limit for the O concentration,[25] 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 characterized by a strong outward relaxation of the surrounding N atoms. The three equivalent N atoms relax by 10.2% (11.8% in Ref. 12) outwards, and the remaining N atom moves 9.5% in [0001] (10.6% in Ref. 12). The formation energy is low (1.6 eV in this work, $\approx$1.3 eV in Ref. 12, and $\approx$1.5 eV in Ref. 17). Oxygen on a nitrogen site has slightly larger Ga-O bonds than the Ga-N bond length in bulk GaN (1.95 Å). We again obtain a low formation energy of 1.7 eV ($\approx$1.7 eV in Ref. 12 and $\approx$1.6 eV in Ref. 17). Bringing V_{Ga}^{3-} and $\mathrm{O_N}^{+}$ together, one obtains $(V_{\mathrm{Ga}}\text{-}\mathrm{O_N})^{2-}$. We find the distance between the vacancy core and O (N) increased by 13.5% (8.9%) which is in good agreement with the values of 14.9% (9.8%) given by Neugebauer and Van de Walle.[12] Furthermore, we determined the energy ΔE for the reaction



$$(V_{\mathrm{Ga}}-\mathrm{O_N})^{2-} \rightarrow V_{\mathrm{Ga}}^{3-} + \mathrm{O_N}^{+},$$

to be 2.2 eV, in good agreement with the plane-wave methods (1.8 eV in Ref. 12 and $\approx$2.1 eV in Ref. 17). We thus obtain 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. 12 and $\sim$0.9 eV in Ref. 17) suggesting a high equilibrium concentration of $\sim 10^{18}/\mathrm{cm}^3$ (Refs. 12 and 17) at a usual MOCVD growth temperature of $\sim$1300 K.

We now investigate V_{Ga}^{3-}, $\mathrm{O_N}^{+}$, and $[V_{\mathrm{Ga}}\text{-}(\mathrm{O_N})_n]^{(3-n)-}$ ($n=1, 2$, and 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,[9] we found the structure of the most stable dislocation to have a closed core (see Fig. 2) consisting of a pair of threefold-coordinated sp^2- (p^3-) hybridized Ga (N) atoms arranged in a dimer as at the $(10\bar{1}0)$ surface.[26] In analogy to the $(10\bar{1}0)$ surface, we found the threading-edge dislocation to be electrically inactive. This is in contrast to full-core screw dislocations which possess very distorted bonds and therefore induce deep states into the band gap.[19] For a detailed discussion of the atomic geometry, electrical properties, and line energy, see Ref. 9.

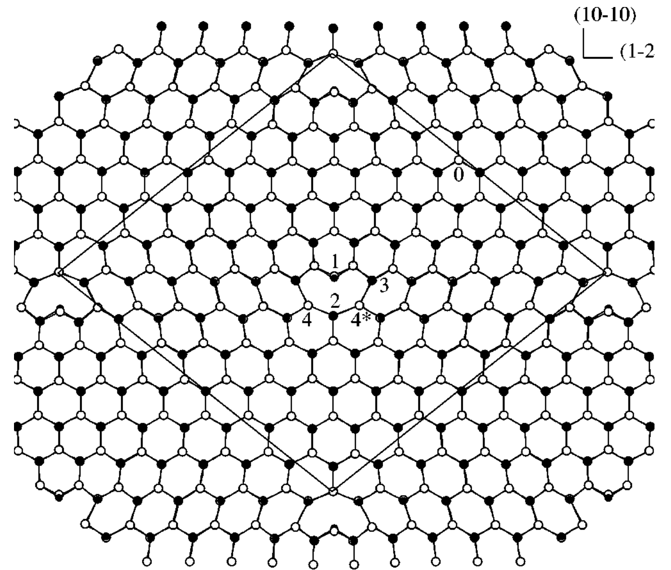


FIG. 2. View along the dislocation line ([0001]) of the 312-atom wurtzite supercell containing a dipole of threading-edge dislocations with Burgers vector $b=[11\bar{2}0]$. White (black) circles represent Ga (N) atoms. Position 0 corresponds to a bulklike region. Position 1 is at the dislocation core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

First, we place the point defects into a bulklike 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

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

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 the first two lines in Table I). We now put the defects at different positions (positions 1, 2, and 3 in Fig. 2) in the dislocation stress field. The resulting formation energies are summarized in Table I. Some of the formation energies are negative, suggesting that under equilibrium conditions the corresponding position would certainly be adopted by the defect. However, since gallium vacancies and oxygen are not necessarily in equilibrium with the dislocation stress field, the precise concentration of defect complexes in the dislocation stress field depends on the history of the sample.

V_{Ga}^{3-} is trapped in the dislocation stress field, in particular, at the dislocation core (position 1 in Fig. 2) and at position 2. Ga atoms in these positions would have high energies, caused by the undercoordination in position 1 or by the strongly strained bonds in position 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 twofold-coordinated N atom which would result in a high energy. However, since Ga atoms at positions 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 threefold coordination. The new configuration has a distorted core and looks like a first step of a kink formation. This suggests that V_{Ga} ehances the formation of kink.

Oxygen atoms sit preferentially twofold or threefold coordinated. This explains why $O_N{}^+$ is more stable by 1.3 eV at the dislocation core (position 1), where it replaces a threefold-coordinated N atom, than in a bulklike region (position 0) where it is fourfold coordinated.

The high stabilities of V_{Ga}^{3-} and $O_N{}^+$ at the dislocation core also imply a very low formation energy for $(V_{Ga}\text{-}O_N)^{2-}$ (−3.3 eV below the energy for position 0). At this position O sits twofold 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 $(V_{Ga}\text{-}O_N)^{2-}$ to be immobile.

Finally, we investigated $[V_{Ga}\text{-}(O_N)_2]^-$ and $V_{Ga}\text{-}(O_N)_3$, which, in analogy to $(V_{Ga}\text{-}O_N)^{2-}$, are found to be particularly stable at the core of the threading-edge dislocations where they are likely to be immobile. This suggests that $[V_{Ga}\text{-}(O_N)_n]^{(3-n)-}$ ($n=1$, 2, and 3) increase the oxygen concentration near to threading-edge dislocations. In contrast to V_{Ga}, the $V_{Ga}-(O_V)_n$ complexes stabilize the dislocation core making it immobile.

The calculations reveal that at bulk positions V_{Ga}^{3-}, $(V_{Ga}\text{-}O_N)^{2-}$, $[V_{Ga}\text{-}(O_N)_2]^-$, and $V_{Ga}\text{-}(O_N)_3$ defects are deep acceptors [with gap states ~1.0–1.2 eV above the valence-band maximum (VBM)]. In order to obtain information about the contribution of these defects to the YL, we then calculated the difference of the formation energies depending on the charge states relevant to the transition in n-type material. The results referenced to the VBM are given in Table II. Subtracting them from the band gap (~3.4 eV) gives a rough estimate for the transition energies in n-type material. Since the energies for the different charge states are derived from total energies associated with a fully relaxed atomic configuration, the calculated energy differences correspond to zero-phonon transitions. As can be seen, at a variety of positions the defects could contribute to the Broad band yellow luminescence. It is interesting to note that in a bulklike position $V_{Ga}\text{-}(O_N)_3$ has a deep gap state (~1.0 eV above the VBM), which comes from a threefold-coordinated nitrogen atom in a bulk position. At the dislocation core (position 1), however, for $V_{Ga}\text{-}(O_N)_3$ all threefold-coordinated nitrogens surrounding the Ga vacancy are replaced by oxygen. At this position we find that $V_{Ga}\text{-}(O_N)_3$ has no deep gap states and does not contribute to the YL.

In conclusion, the density-functional calculations show that in wurtzite GaN the stress field of threading-edge dislo-

TABLE II. Transition energies of V_{Ga}, $V_{Ga}\text{-}O_N$, $V_{Ga}\text{-}(O_N)_2$, and $V_{Ga}\text{-}(O_N)_3$ at the threading-edge dislocation (see Fig. 2) referenced to the VBM).

Position	$E^{2-/3-}$ (V_{Ga})	$E^{1-/2-}$ $(V_{Ga}\text{-}O_N)$	$E^{0/1-}$ $(V_{Ga}\text{-}O_{2N})$	$E^{1+/0}$ $(V_{Ga}\text{-}O_{3N})$
position 0 (bulklike)	1.4	1.0	0.7	0.9
position 1 (core)	0.8	1.0	0.7	0.4
position 2	0.4	0.3	0.6	0.8
position 3	0.8	1.4	1.0	0.9

cations 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 twofold coordinated with very strong Ga-O bonds and is therefore immobile. Following previous studies,[12,17] we find that the gallium vacancy- and oxygen-related defect complexes are electrically active and suggest that they increase the intensity of the broad band yellow luminescence near threading-edge dislocations, consistent with cathodoluminescence studies.[4]

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