

Kinetic path towards the passivation of threading dislocations in GaN by oxygen impurities

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Defect tolerance can be critically important for optoelectronics. GaN, specifically, tolerates a relatively large concentration of threading dislocations, but the physical origin of this tolerance remains a mystery. First-principles calculations reveal the removal of deep-level states from edge dislocations by oxygen passivation. This removal is, however, not a thermodynamic ground state but kinetically driven. Oxygen incorporation during growth can be harmful; it becomes beneficial if introduced in the cooling-down phase or post-growth thermal treatment at a significantly lower temperature. Our findings extend first-principles defect study to the nonequilibrium regime where low-diffusion-barrier defects affect electronic behavior of semiconductors in unexpected fashion.

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GaN is a wide-gap semiconductor commonly used for optoelectronics such as blue LEDs/lasers and for power electronics and radiation hardened electronics [1,2]. Unlike other more traditional semiconductors, however, there is no adequate substrate that is lattice matched to GaN. The GaN epitaxial thin films therefore often contain large densities of dislocations, despite the number of techniques, such as lateral epitaxial overgrowth [3], hydride vapor-phase epitaxy [4], and stress control [5], that have been developed to reduce the density of the dislocations. Yet, in sharp contrast to other semiconductors, a GaN device can operate with several orders of magnitude higher dislocation density than, for example, GaAs or InP [6]. This unique tolerance to extended defects [7] holds the key to the success of GaN. The microscopic origin for such a remarkable defect tolerance is, however, unclear or even controversial. It has been argued that dislocations in GaN should have similar electronic properties to GaN surfaces. Since it has been observed that the GaN surfaces do not exhibit Fermi-level pinning, they were postulated to lack mid-gap states [6,7]. However, first-principles calculations for numerous dislocations, including partial dislocations [8,9], threading edge [10,11], screw [12], and mixed [13,14] dislocations, have shown that these dislocations all have deep-level states. Hence, GaN may not be immune to nonradiative recombination of its free carriers at its dislocations.

Adding to the complexity of GaN is another important factor: the presence of unavoidable and unintentional impurities. In GaN films grown by MOCVD and HVPE, oxygen is among the most common ones, with the lowest-energy configuration of O in bulk GaN being a substitution for an N atom within the lattice, O_N [15]. In the presence of a dislocation, which could add an additional degree of freedom to relax the O_N , a lowering of the oxygen formation energy seems to be likely. In other words, interactions between point defects and dislocations are inevitable and even energetically favored [16]. On the experimental side, it has been shown that dislocations in GaN cause O segregation [8,17–19], as well as enhancing O diffusion [20,21]. Recently, O annealing was found to increase the electrical performance of AlGaIn/GaN, which has been attributed to an O passivation effect of the dislocations [22]. These observations raise the question: Can interaction with

O offer a clue to the exceptional dislocation tolerance of GaN? Since the most common type of dislocation observed for *c*-plane growth in GaN is the threading edge dislocation [23], among which is the 5/7-atom ring core structure, with alternating Ga-Ga and N-N homopolar (wrong) bonds, is found to be experimentally and theoretically most stable [24–26], the question then becomes: Will unintentional O passivate the edge dislocations? Clearly, the answer to such a question can be important to GaN and other vital optoelectronic materials.

In this Rapid Communication, we perform first-principles calculations of O interaction with threading edge dislocations with a low-energy 5/7-atom ring core. The results point to the possibility of passivation of mid-gap states of the dislocation by O, thereby providing a plausible mechanism for defect tolerance in GaN. In particular, each O interstitial, O_i (DL), eliminates one Ga-Ga wrong bond at the core of the dislocation (DL), along with its deep-level state. Unlike traditional defect theory, here the oxygen's effect depends on the experimental conditions: During growth, O favors the substitutional N site to create half-occupied and harmful deep-level states. To passivate the edge dislocations, the formation of O_N (DL) has to be kinetically prohibited due to the high energy barrier and the Ga supply needs to be removed (i.e., post-growth processing) so it no longer reacts with O to form Ga_2O_3 . The latter results in an exothermic formation of O_i (DL) at the 5/7-atom ring core via an in-diffusion of O atoms through the dislocation core with a barrier of only 1.2 eV. Hence, dislocation passivation by O can be easily achieved in air, e.g., during the cooling-down phase or due to any post-growth thermal treatment of the samples. In principle, the nonequilibrium approach developed here should apply to interstitials, and for that matter, other low-diffusion-barrier defects, in a broad range of electronic materials.

Our calculations are performed using density functional theory (DFT) [27,28] within the Perdew-Burke-Ernzerhof (PBE) approximation [29] for the exchange-correlation functional. The core-valence interactions are described by the projector augmented-wave (PAW) potentials, as implemented in the VASP code [30]. Plane waves with a kinetic energy cutoff of 345 eV are used as the basis set. Test calculations at an energy cutoff of 400 eV show a difference of less than 0.1 eV in the formation energies. A large 760-atom, 4.4 nm diameter nanowire (including passivating surface pseudo-H atoms) is relaxed by force minimization until the energy

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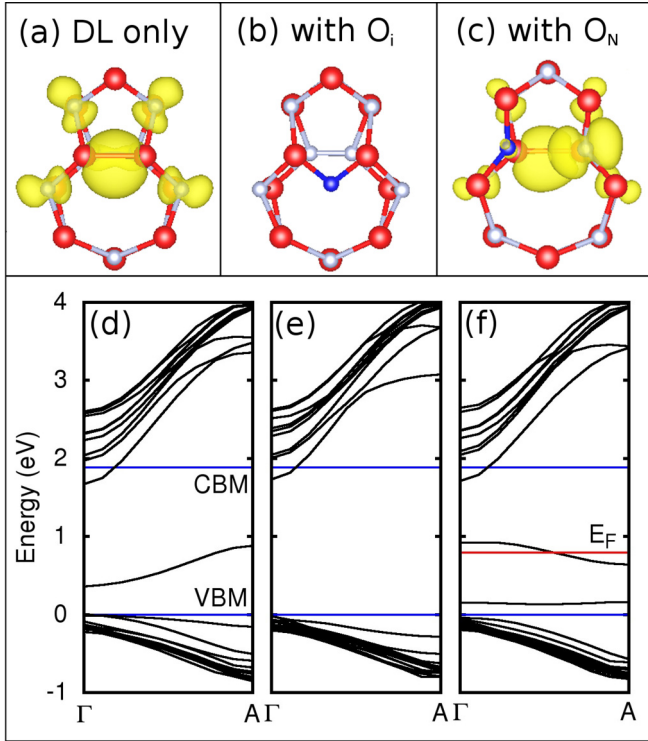


FIG. 1. (a)–(c) Atomic structure of 5/7-atom ring dislocation core with and without O atom. Ga is red, N is light blue, and O is dark blue. Yellow regions indicate charge density isosurfaces from the deep level. (d)–(f) The corresponding band structures. Positions of the bulk GaN band edges are marked by horizontal lines. The band structure for (f) changes when considering spin polarization; see Fig. S4 in the Supplemental Material [31].

difference is less than 0.1 meV and the forces on the atoms are less than 0.05 eV/Å. Further details of the nanowire model calculation are presented in Fig. S1 in the Supplemental Material [31]. The diffusion of O atom is studied using the nudged elastic band (NEB) method within the climbing image approximation [32]. In the diffusion calculation, it is necessary to reduce the nanowire diameter to allow for doubling the supercell in the direction parallel to dislocation core. The reduced diameter is about 1.7 nm, and the nanowire contains 132 Ga and N atoms. The k -point meshes of $1 \times 1 \times 3$ and Γ only are used for the Brillouin zone integration of the reduced and large nanowires, respectively. Hybrid functional calculations (shown in Fig. S2 in the Supplemental Material [31]) confirm our conclusions based on PBE. To verify that the dislocation-surface interaction in our nanowire model is small, calculations based on the dislocation dipole model by Sidney Yip [33] have been carried out (Fig. S3 in the Supplemental Material [31]). Both methods yield the same defect formation energy and electronic properties.

Figure 1(a) shows the core structure of the 5/7-atom ring edge dislocation which breaks the pattern of 6-atom hexagonal rings (as viewed along the c axis) by creating adjoined 5-atom and 7-atom rings. At the point where these two rings touch, there is a column of alternating Ga-Ga and N-N wrong bonds. Our calculations have found the two most stable configurations for O segregation at the dislocation core, i.e., the interstitial

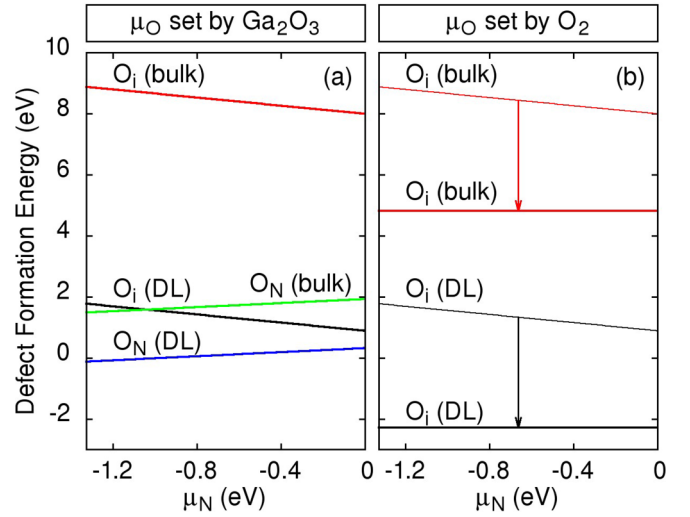


FIG. 2. Defect formation energy under different experimental conditions. (a) Under thermal equilibrium with secondary Ga₂O₃ phase [cf. Eq. (3)] and (b) in the absence of secondary phase due to the removal of Ga supply. Arrows show the subsequent drop of O interstitial energies.

oxygen O_i(DL) and the substitutional oxygen O_N(DL) in Figs. 1(b) and 1(c), respectively. Each forms a line defect along the core of the dislocation, one O per unit length (5.17 Å). The O_i(DL) breaks the Ga-Ga wrong bond by forming a bond to each of the Ga atoms. As a result, the Ga-Ga distance increases from 2.26 Å to 2.68 Å. In contrast, the N-N wrong bond, which was at 1.55 Å, changes by less than 0.01 Å. For the substitutional O_N(DL), the distance between atomic N-N columns increases from the original distance of 1.55 Å to the O-N distance of 2.82 Å, so the wrong bond no longer exists. In contrast, the Ga-Ga wrong bond does not break, but is elongated by 7% from 2.26 Å to 2.41 Å.

The formation energy E_{form} for a neutral defect X is calculated by [34]

$$E_{\text{form}}[X] = E_{\text{tot}}[X] - E_{\text{tot}}[\text{host}] - \sum_i n_i \mu_i, \quad (1)$$

where μ_i are the chemical potentials of individual atomic species, and n_i are the number of atoms added to ($n_i > 0$) or removed from ($n_i < 0$) the host to form defect X . The values of μ_i are constrained by the precipitation of the elemental Ga solid and gas N₂ phase, and the thermal equilibrium with GaN, i.e.,

$$\mu_N + \mu_{\text{Ga}} = \mu_{\text{GaN}}. \quad (2)$$

During the growth of GaN, μ_O is also affected by the formation of secondary phases such as Ga₂O₃, i.e.,

$$2\mu_{\text{Ga}} + 3\mu_O \leq \mu_{\text{Ga}_2\text{O}_3}. \quad (3)$$

Figure 2(a) shows the energies of O impurities as a function of μ_N , calculated based on Eqs. (1)–(3). In bulk GaN, the most stable O impurity is substitutional O [O_N(bulk)]. An interstitial O is typically 6 eV higher in energy. In the presence of the 5/7-atom ring dislocation, however, the formation energies of the O impurities are lowered considerably, by about 2 eV for O_N and by almost 7 eV for O_i, indicating that oxygen

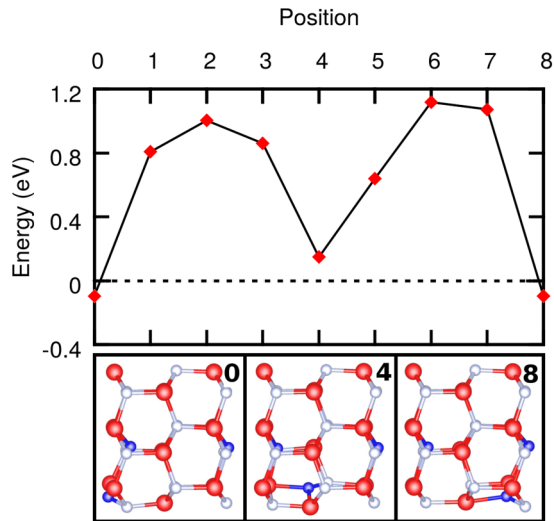


FIG. 3. Energy profile for the diffusion of an O atom along an already-oxidized dislocation core. Panels at the lower half show the oxygen positions and atomic structures of the surrounding atoms. The dashed line corresponds to the chemical potential of O_2 in vacuum. Atoms are colored as in Fig. 1.

should be preferentially incorporated into regions near the dislocation core. Despite the energy changes, $O_N(\text{DL})$ is still noticeably lower in energy than $O_i(\text{DL})$. In contrast, Fig. 2(b) shows a different scenario where the constraint set by Eq. (3) is lifted. This raises the upper bound on μ_O considerably such that the formation of interstitial $O_i(\text{DL})$, at -2.3 eV, becomes energetically favorable. In principle, the change in μ_O should affect the formation energy of all O impurities. However, converting an $O_i(\text{DL})$ to $O_N(\text{DL})$ requires the formation of a $V_N - N_i(\text{DL})$ Frenkel pair, which is both energetically costly and kinetically difficult. The formation energy of the Frenkel pair with N_i at the dislocation core is 1.9 eV. Adding the kinetic barrier would further increase the energy due to the fourfold coordination of the N atom. Therefore, formation of $O_N(\text{DL})$ at the expense of $O_i(\text{DL})$ at a temperature significantly lower than the growth temperature is highly unlikely.

While the above analysis is instructive, it is still a question how the O interstitials travel to the dislocation core, since $O_i(\text{bulk})$ formation remains at least 5 eV even when the Ga supply is removed. The hint comes from the experimental fact that oxygen can diffuse through dislocations [20,21]. Since threading dislocations typically end at surfaces, oxygen atoms may diffuse through the dislocation core and remove nonoxidized Ga-Ga wrong bonds along the way. To examine such a scenario, we build a $2 \times$ supercell along the dislocation line where the core is fully oxidized by O atoms. Using the NEB method, we calculate the diffusion of an additional O atom. This way, an upper bound for the O diffusion barrier may be estimated. The calculated energy profile is shown in Fig. 3 in the upper panel, whereas three snapshots of the atomic positions at the start (frame 0), in the middle (frame 4), and at the end (frame 8) of the O diffusion are shown in the lower panels. It is interesting to note that the nonbonded oxygen atom, i.e., the diffusing O at the bottom of the lower panels in Fig. 3, is spontaneously attracted to the dislocation core as it has an energy lower than forming an O_2 in vacuum.

It prefers to stick to the side wall of the 7-membered ring by displacing N atoms to co-share Ga atoms. A diffusion barrier of 1.2 eV is obtained from the NEB calculation. It corresponds to a diffusion rate at 600 K of 8×10^2 jumps per second with an attempt frequency of 10^{13} per second [35]. In experiments, O annealing temperature can be higher [22]. Hence, one can eliminate Ga-Ga wrong bonds in the 5/7-atom ring dislocations by oxygen after growth. Once the diffusing O atom reaches a nonoxidized Ga-Ga wrong bond, it will spontaneously insert into the bond, lowering its energy by about 2.2 eV [cf. Fig. 2(b)].

Figures 1(d)–1(f) show the band structure. The bare dislocation core in Fig. 1(d) has doubly-occupied deep-level states, which can trap carriers and cause nonradiative recombination. The charge contour plot in Fig. 1(a) shows that this deep level originates from the Ga-Ga wrong bond. As the insertion of the interstitial $O_i(\text{DL})$ to the dislocation core breaks the Ga-Ga wrong bond, not surprisingly, the defect state is removed, as can be seen in Fig. 1(e). In contrast, the formation of $O_N(\text{DL})$ alters the dispersion of the deep level but does not remove it. It also changes the occupation of the gap state, though in a nonintuitive way. In bulk GaN, the O_N is a shallow donor which should place the Fermi level near the bottom of the conduction band. Instead, here it halfway empties the defect level, as can be seen in Fig. 1(f).

The qualitative results can be understood based on the electron counting model (ECM) [36]. Since, in the wurtzite structure, the Ga atom (valence 3) and N atom (valence 5) are both fourfold coordinated, each Ga- and N-dangling bond has $3/4$ and $5/4$ electrons, respectively. Therefore, each Ga-Ga wrong bond should have $3/4 + 3/4 = 1.5$ electrons whereas each N-N wrong bond should have $5/4 + 5/4 = 2.5$ electrons. The ECM states that each bond should host two electrons. A transfer of 0.5 electrons from N-N to Ga-Ga would make the Ga-Ga wrong bond host $1.5 + 0.5 = 2$ electrons and the N-N wrong bond also host $2.5 - 0.5 = 2$ electrons. This means that the deep level at the dislocation core should be a doubly-occupied weak Ga-Ga bond, as confirmed by Fig. 1(a). After the insertion of $O_i(\text{DL})$ atoms along the dislocation core, each $O_i(\text{DL})$ atom grabs two electrons, one from each surrounding Ga atom. This replaces the Ga-Ga wrong bond by two stronger Ga-O bonds whose electronic states are buried deep inside the valence band. In contrast, the replacement of the N atom at the dislocation core by $O_N(\text{DL})$ breaks the anion-anion wrong bond, as mentioned before. It leaves behind a threefold coordinated N with a doubly occupied lone-pair state and, separately, a threefold coordinated O with also a doubly occupied lone-pair state. There are, however, only three electrons available, which are the two electrons from the original N-N wrong bond and the extra electron from the O replacing N, so they must get another electron from the occupied high-lying defect state. This leaves a singly-occupied Ga-Ga deep-level state inside the band gap, as depicted in Fig. 1(f). Two more common impurities in GaN, hydrogen and sulfur, were also tested as passivants in GaN dislocations (see Fig. S5 of the Supplemental Material [31]); however, neither remove the gap states as O_i does. Hydrogen fails to passivate the dislocation because two H atoms would be required by the ECM to break the Ga-Ga wrong bond, but instead the two spontaneously form an H_2 molecule. Sulfur does remove

the occupied defect state similar to oxygen, but its p states are higher in energy than oxygen and reside inside the band gap. As other impurities would have an incorrect valency or higher-energy p states, oxygen is unique in passivating the most common dislocation in *c*-plane GaN.

We note that the pioneer first-principles study of dislocation with impurities, particularly with O impurity, was carried out in 1998 [37] in the context of substitutional O and Ga vacancy, O_N-V_{Ga} , pairs. However, the 8-membered ring dislocation core structure used there was later found to be too high in energy [24]. It is interesting, though, that our $O_i(DL)$ structure is similar to one of their structures, but their conclusion was opposite to ours, as the O_N-V_{Ga} complexes were calculated to be deep-level defects responsible for yellow luminescence [37,38]. Even the oxygen impurity, which is structurally identical to our $O_i(DL)$, is a deep donor with a (0/+) level 0.4 eV above the valence band maximum (VBM). We found, however, that this level position is an artifact of calculating an array of overly dense and infinitely-long *charged* lines in the supercell approximation. Physically, charged defects on a dislocation line must be far apart, i.e., at the dilute limit, to avoid their mutual repulsion and the subsequent logarithmic divergence. Due to the use of a small supercell and the compensating charge (known as the jellium background), the energy of the isolated charged defect is underestimated from

its dilute limit [39]. As we increase the separation between charged O_i atoms along the dislocation core, the deep (0/+) transition level disappears, as a result of the increased energy for (+)-charge defect, so O passivation of the deep-level dislocation states is indeed physically correct.

In summary, first-principles calculations reveal that deep-level edge dislocation states in GaN can be totally removed by interstitial oxygen. However, the behavior of the O at a dislocation core can be complex due to various experimental conditions, leading to conflicting results and interpretations. To understand the oxygen interaction with edge dislocations, a kinetic theory is developed. Detailed NEB calculation reveals that at modest temperature, oxygen in-diffusion along the dislocation core of GaN readily takes place, in agreement with experiments. While our theory points to a possible explanation of the dislocation tolerance of GaN, the implications go beyond just one material by shedding light on the mechanisms of electrically inactive dislocations in other semiconductors. More broadly, our nonequilibrium approach applies to other low-diffusion-barrier defects in electronic and optoelectronic applications.

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