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Interaction of Oxygen with Threading Dislocations in GaN

R. JONES (a), J. ELSNER (a), M. HAUGK (b), R. GUTIERREZ (b),
TH. FRAUENHEIM (b), M. I. HEGGIE (c), S. ÖBERG (d), and P. R. BRIDDON (e)

(a) *Department of Physics, University of Exeter, Exeter, EX4 4QL, UK*

(b) *Theoretische Physik III, Technische Universität, D-09107 Chemnitz, Germany*

(c) *CPES, University of Sussex, Falmer, Brighton, BN1 9QJ, UK*

(d) *Department of Mathematics, University of Luleå, Luleå, S97 187, Sweden*

(e) *Department of Physics, University of Newcastle upon Tyne, Newcastle, NE1 7RU, UK*

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A review is given of the results of first principles calculations used to investigate the structures and electronic properties of screw and edge dislocations in GaN. The atoms at the core of the full core screw dislocation possess heavily strained bonds leading to deep gap states. Removing the first shell of Ga and N atoms gives a screw dislocation with a small open core consisting of $\{10\bar{1}0\}$ type surfaces. Therefore open-core screw dislocations induce only shallow gap states. In the same way we found the core of the threading edge dislocation to be reconstructed without any deep states. The interaction of oxygen with the cores of open-core screw and edge dislocations is considered and it is found that the impurity has a strong tendency to be bound by Ga vacancies leading to three types of defect trapped in the strain field. We suggest that the most stable defect leads to a poisoning of growth centres on the walls of nanopipes.

1. Introduction

Dislocations in hexagonal GaN are quite unlike those in other III–V materials like cubic GaAs. For example, the screw dislocation in GaN [1 to 3] lies along $[0001]$ with a full Burgers vector $\mathbf{b} = c[0001]$, whereas in Si or GaAs [4 to 6], it lies along $[1\bar{1}0]$ and is dissociated into 30° partials with $\mathbf{b} = (a/6)[2\bar{1}\bar{1}]$. The core structures of the dislocations are also quite different. In the case of GaAs, dislocations are believed to lie on the glide set of planes with a non-stoichiometric core structure consisting of two adjacent chains of chemically identical atoms. Previous calculations [7] indicate that, in the 90° partial, bonds between atoms of the same type are formed in a similar way with the reconstructions in anti-site defects. The latter appear to have relatively low formation energies in GaAs, unlike GaN. The reconstruction between like atoms in GaAs is, however, relatively weak. This explains the lower activation energies for dislocation motion in GaAs than, say, in Si, and the reconstruction is easily broken or affected by impurities. On the other hand, the core of the open-core screw dislocation in GaN is stoichiometric with a structure similar to that of the $(10\bar{1}0)$ surface, where Ga and N atoms assume positions determined by the transfer of charge from Ga to lone pairs on N. Such a relaxation leads to the removal of deep states from the band gap. Similarly, edge dislocations undergo a relaxation also eliminating deep states from the band gap.

Only the full core screw dislocation in GaN possesses very distorted bonds at the core and therefore induces deep states in the band gap. Thus, in spite of the differences in bonding and dislocation type and Burgers vector – whose main effect is to make dislocations immobile in GaN – the electronic structures of the cores of dislocations in GaAs and GaN are similar in that, except for the GaN full core screw dislocation, deep states are eliminated from the gap. Dislocations in both materials have one other important common feature: they both interact very strongly with impurities and intrinsic defects. Such interactions often induce an electrical activity and this is perhaps their most important property.

Growth of GaN on sapphire by vapour phase epitaxy is often associated with the appearance of long nanopipes parallel to $\mathbf{c}$ which have hexagonal cross sections with uniform diameters ranging from 50 to 250 Å [8]. The first suggestion was that they were the manifestation of screw dislocations with empty cores as discussed by Frank long ago [9]. However, our calculations do not support the idea that the core of a screw dislocation with Burgers vector equal to $\mathbf{c}$ is open with such a large diameter [10]. On the other hand, Liliental-Weber et al. [11] have found that the density of nanotubes is increased in the presence of impurities, e.g. O, Mg, In, and Si and have argued that these impurities decorate the $\{10\bar{1}0\}$ type walls of the nanotubes inhibiting overgrowth. This is an idea that we shall discuss in some detail.

GaN is important because of its optoelectronic properties characterised by a wide band gap of 3.4 eV, but defect-induced electronic states in the band gap can significantly degrade the optical performance. The most commonly observed defect emission in n-type wurtzite GaN grown on sapphire, the yellow luminescence (YL) is centred at 2.2 to 2.3 eV with a line width of ≈ 1 eV. It is not present in cubic material grown on GaAs [12]. 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 [13], or a deep donor and a shallow acceptor [14]. Recent work has, however, found evidence for the deep acceptor model [15]. 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 [16].

The most likely acceptor is an intrinsic defect like a Ga vacancy, V_{Ga} , probably complexed with an impurity. V_{Ga} , or vacancy complexes, have been detected by positron annihilation studies in bulk GaN and their concentration was found to be related to the intensity of the YL [17]. Theory has suggested that V_{Ga} is a triple acceptor with the $(- - - / - -)$ level at $\approx E_v + 1.1$ eV [18]. This suggests that V_{Ga} forms defect complexes with oxygen which might be involved in the YL [18, 19]. Atomic force microscopy in combination with CL has led to the conclusion that threading edge dislocations act as non-radiative recombination centres and degrade the band edge emission [20].

The structure and electronic properties of dislocations and their defects in GaN have been found, using both an ab initio local density functional (LDF) cluster method, AIMPRO [21], and a self-consistent charge density functional based tight binding method SCC-DFTB [22]. Isotropic elasticity theory was used to generate the initial positions of the atoms. In the AIMPRO case dislocations were modelled in H terminated clusters. For example, the pure dislocations were modelled with 392 atom stoichiometric clusters. In the SCC-DFTB case the dislocations are modelled in 210 atom clusters periodic along the dislocation line as well as in 312 atom supercells containing disloca-

tion dipoles. The supercell calculations allow the formation energies of oxygen defects to be calculated assuming that they are in equilibrium with Ga_2O_3 . Relaxation of the clusters or unit cells were then carried out using the conjugate gradient algorithm.

In Section 2 we discuss the structure and properties of the pure dislocations while in Section 3, we deal with the interaction of oxygen with the cores of open-core screw and edge dislocations.

2. Dislocations in GaN

2.1 Screw dislocations

We consider first a screw dislocation with a full core [10]. Full-core screw dislocations have recently been observed by Xin et al. [23] using the high resolution Z -contrast imaging technique. The presence of atoms so close to the dislocation axis leads to severely strained bond lengths distorted by as much as $0.4 \text{ \AA}$. Consequently it is not surprising that such dislocations possess deep gap states ranging from $E_v + 0.9 \text{ eV}$ to $E_v + 1.6 \text{ eV}$ and shallow states around $E_c - 0.2 \text{ eV}$. An analysis of these gap states revealed that the states above E_v are localised on N core atoms, whereas those below E_c are localised on both Ga and N core atoms. The strong distortion of the bonds of the core atoms leads to a high line energy within our calculations.

A similar calculation was then carried out with the hexagonal core of the screw dislocation removed giving a core with a narrow opening of $\approx 7.2 \text{ \AA}$. Figs. 1 and 2 demonstrate that the resulting core consists of $\{10\bar{1}0\}$ type facets except for the topological singularity required by a Burgers circuit. The atoms on these walls adopt threefold coordinations similar to those found on the $(10\bar{1}0)$ surface. Thus, Ga (N) atoms develop sp^2 (p^3) hybridisations which lower the surface energy and clean the gap [24]. However, in contrast to the $(10\bar{1}0)$ surface, the open-core dislocation appears to possess shallow gap states. In the open-core dislocation, bonds are distorted less than in the full-core and by only about $0.1 \text{ \AA}$. The calculated line energy is also slightly lower than that found for the full-core screw dislocation. Removing further material from the core resulted in a higher line energy and thus we conclude that the equilibrium diameter is about $7.2 \text{ \AA}$. The relatively small line energy difference found between full-core and

Fig. 1. Top view (in $[0001]$) of the screw dislocation with a narrow opening ($d \approx 7.2 \text{ \AA}$). The threefold coordinated atoms 1 (Ga) and 2 (N) adopt a hybridization similar to the $(10\bar{1}0)$ surface atoms

Fig. 2. Projection of the wall of the open-core screw dislocation

open-core ($d \approx 7.2 \text{ \AA}$) screw dislocations suggests a shallow minimum which probably allows all intermediate structures to exist. In our calculations only structures constructed by removing entire hexagons, but not those obtained by removing single rows were considered. Calculating the latter ones, may lead to slightly lower energies. We note that our calculations allow only diameters very much smaller than the diameter of nanopipes and we suppose that their formation is not due to Frank's mechanism.

2.2 Edge dislocations

The relaxed core of a threading edge dislocations with Burgers vector $a[\bar{1}210]/3$ is shown in Fig. 3. It consists of a line of Ga and N atoms which have threefold coordination. With respect to the perfect lattice the distance between columns (1/2) and (3/4) (and the equivalent on the right) are 9% contracted while the distance between columns (9/10) and (7/8) (and the equivalent on the right) are 13% stretched. This atomic geometry for the threading edge dislocation has recently been confirmed by Xin et al. [23] using atomic resolution *Z*-contrast imaging. Consistent with our calculation they determined a contraction (stretching) of $(15 \pm 10)\%$ of the distances between the columns at the dislocation core. The threefold coordinated Ga (N) atoms (labelled 1 and 2 in Fig. 3) move in such a way to enhance sp^2 and p^3 hybridisation, respectively. This leads to empty Ga lone pairs pushed towards E_c , and filled lone pairs on N atoms lying near E_v , in a manner identical to the (10 $\bar{1}$ 0) surface. Thus threading edge dislocations are then also electrically inactive except possibly for shallow levels. It seems that the small bond distortions within the core makes it energetically uneconomical for the core of the threading edge dislocation to be open. We obtain a line energy for the edge

Fig. 3. Top view (in [0001]) of the relaxed core of the threading edge dislocation. This geometry has recently been confirmed using the atomic resolution *Z*-contrast imaging technique [23]. The threefold coordinated atoms 1 (Ga) and 2 (N) adopt a hybridization similar to the (10 $\bar{1}$ 0) surface atoms

dislocation which is by more than a factor of two lower than that found for the screw dislocation. This is mainly due to the lower elastic energy arising from the Burgers vector.

In AlN, Wright and Furthmüller [25] have found, using a supercell geometry, that edge dislocations have an empty band of levels $\approx E_c - 2$ eV, while in n-type material, the core contains V_{Al} defects. The very much larger band gap of this material might be responsible for the differences of the properties of the edge dislocations from those in GaN.

To summarise, the density functional calculations reveal that the threading screw dislocations in their pure, i.e. impurity free form can exist with full cores and narrow open cores with diameters up to ≈ 7.2 Å. While full-core screws are electrically active, open-core screws induce no deep gap states. Threading edge dislocations in wurtzite GaN are stable with full cores and electrically inactive. However, the strained and ‘dangling’ bonds present in their cores could permit impurities and intrinsic defects to be trapped there.

3. Interaction of Oxygen with Dislocations

3.1 Oxygen and open core screw dislocations

There is experimental evidence that oxygen acts as a donor in bulk GaN [26] and total energy calculations show that O sits on a N site [27]. Since the internal surfaces of screw dislocations are very similar to those of the low energy $(10\bar{1}0)$ surface, we investigated [28] the likely surface sites for oxygen replacing N atoms. We found that the energy of a neutral O_{N} defect is 0.8 eV lower at the relaxed $(10\bar{1}0)$ surface. This shows that there is a tendency for O to segregate to the surface. The added oxygen has an additional electron occupying a state near E_c . The defect has therefore a high energy and would attract acceptors resulting in a neutral complex. One possible acceptor, other than added dopants, would be a gallium vacancy (V_{Ga}) which acts as a triple acceptor and has been calculated to have a low formation energy in n-type GaN [18, 29]. Consequently, we suppose that the surface oxygen concentration could be sufficiently large, and the oxygen atoms sufficiently mobile, that the three N neighbours of V_{Ga} at the $(10\bar{1}0)$ surface are replaced by O forming the $V_{\text{Ga}}-(O_{\text{N}})_3$ defect.

Our calculations [28] showed that $V_{\text{Ga}}-(O_{\text{N}})_3$ is more stable at the surface than in the bulk by 2.2 eV. Two O neighbours of the surface vacancy lie below the surface and each is bonded to three Ga neighbours, but the surface O is bonded to only two subsurface Ga atoms in a normal oxygen bridge site. The defect is electrically inactive with the O atoms passivating the vacancy in the same way as VH_4 in Si.

The question then arises as to the influence of the defect on the growth of the material. Growth over the defect must proceed by adding a Ga atom to the vacant site but this leaves three electrons in shallow levels near the conduction band resulting in a very high energy. This suggests that the defect can stabilise the surface and thus inhibit growth. From this we can conclude that such defects lead to the formation of nanpipes if we assume that during growth of the epilayers, either nanpipes with very large radii are formed which gradually shrink when their surfaces grow out, or there is a rapid drift of oxygen to a pre-existing nanpipe. In either case the concentration of oxygen and $V_{\text{Ga}}-(O_{\text{N}})_3$ defects increases at the walls of the nanpipe. The maximum concen-

tration of this defect would be reached if 50% (100%) of the first (second) layer N atoms were replaced by O and further growth then would be prevented. It is, however, likely that far less than the maximum concentration is necessary to stabilise the surface and make further shrinkage of the nanopipe impossible. Provided oxygen could diffuse to the surface fast enough, the diameter and density of the holes would be related to the initial density of oxygen atoms in the bulk. This model requires that the walls of the nanopipe are coated with oxygen although the initial stages of formation of the pipe are obscure.

In conclusion, we have shown that oxygen has a tendency to segregate to the $(10\bar{1}0)$ surface and forms stable and chemically inert $V_{Ga}-(O_N)_3$ defects. These defects increase in concentration when the internal surfaces grow out. When a critical concentration of the order of a monolayer is reached, further growth is prevented. This model leads to nanopipes with $\{10\bar{1}0\}$ type walls coated with GaO and supports the suggestions of Liliental-Weber et al. that nanopipes are linked to the presence of impurities [11].

3.2 Oxygen and edge dislocations

The $V_{Ga}-(O_N)_3$ defect considered above is electrically inactive at a $(10\bar{1}0)$ surface site but defects like $V_{Ga}-(O_N)_2$ and $V_{Ga}-O_N$ act as single and double acceptors, respectively. If these were trapped in the strain field of a dislocation, then we would expect the dislocation to appear electrically active [30].

V_{Ga}^{3-} , O_N^+ , $(V_{Ga}-O_N)^{2-}$, $(V_{Ga}-(O_N)_2)^-$ and $V_{Ga}-(O_N)_3$ defects were first placed far away from the dislocation core in a 624 atom supercell (i.e. the 312 atom supercell was doubled along $[0001]$) containing an edge dipole. Their energies were then compared with the same defects sited within the core. The core site for V_{Ga}^{3-} and O_N^+ corresponded to the replacement of the threefold coordinated Ga or N core atoms, respectively. The energies of each of these defects were lower at the dislocations by ≈ 1.6 eV. The energy of $V_{Ga}-(O_N)_n$ is much lower at the dislocation core than in the bulk. This is because a neighbouring pair of threefold coordinated Ga and N atoms are removed from the core and an O atom is inserted into the N site. The oxygen atom then lies in bridge site between two Ga atoms in a normal bonding configuration. The resulting formation energies of these defects lie between -2 and -3 eV (Table 1). Thus the core of the dislocation will spontaneously oxidise if oxygen is mobile. In any event, we anticipate that the core will contain electrically active donor and acceptor pairs possibly giving rise to the broad band yellow luminescence.

Table 1

Formation energies in eV of V_{Ga}^{3-} , O_N^+ , $(V_{Ga}-O_N)^{2-}$, $(V_{Ga}-(O_N)_2)^-$ and $V_{Ga}-(O_N)_3$ defects at bulk-like sites and within the core of a threading edge dislocation. The calculations were carried out assuming Ga-rich growth conditions, O in equilibrium with Ga_2O_3 and n-type material

position	bulk-like site	core site
V_{Ga}^{3-}	1.7	-0.2
O_N^+	1.5	0.2
$(V_{Ga}-O_N)^{2-}$	1.0	-2.3
$(V_{Ga}-(O_N)_2)^-$	0.9	-2.5
$V_{Ga}-(O_N)_3$	0.7	-3.0

In conclusion, the density functional calculations show that in wurtzite GaN the stress field of threading edge dislocations is likely to trap gallium vacancies and oxygen as well as their complexes. 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 [16].

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