Effect of oxygen on the growth of $(10\bar{1}0)$ GaN surfaces: the formation of nanopipes

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Abstract

Local density–functional methods are used to examine the behavior of O and O related defect complexes on the walls of nanopipes in GaN. We find that O has a tendency to segregate to the $(10\bar{1}0)$ surface and identify the gallium vacancy surrounded by three oxygen impurities (V_{Ga}–$(O_N)_3$) to be a particularly stable and electrically inert complex. We suggest that during Stranski-Krastanow growth, when inter-island spaces shrink, these defects reach a critical concentration beyond which further growth is prevented and nanopipes are formed.

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Growth of GaN on sapphire by vapor phase epitaxy is often associated with the appearance of long nanopipes parallel to **c**. They occur at a density $\sim 10^8$ cm^2 and have hexagonal cross sections with constant diameters ranging from 50–250 Å [1–3]. The first suggestion was that they were the manifestation of screw dislocations with empty cores as discussed by Frank long ago [4]. However, *ab initio* calculations do not support the idea that the core of a screw dislocation with Burgers vector equal to **c** is open with such a large diameter [5]. Pirouz [6] has argued that superscrew dislocations with Burgers vectors $n\mathbf{c}$ with $n > 1$ are formed during growth by the collision of islands. Clearly, if n were big enough, then the cores would be open. However, there is at present no microscopic evidence for such dislocations [7]. On the other hand, Liliental-Weber *et al.* [8] 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 $(10\bar{1}0)$ walls of the nanotubes inhibiting overgrowth. In this paper, we discuss in some detail the nature of the oxygen defects needed to inhibit growth.

There are two types of $(10\bar{1}0)$ surfaces (see Fig. 1), the N and Ga atoms on the ideal surfaces having either one (Type I in Fig. 1) or two (Type II in Fig. 1) dangling bonds. Surfaces of type I have a lower surface energy and will thus be considered in the following. Relaxation occurs leading to sp^2 (sp^3) hybridized Ga (N) surface atoms with a charge transfer from the surface Ga to the surface N atom. This results in empty Ga dangling bonds and filled N lone pairs and a semiconducting surface [9].

Consider now an O atom replacing a N atom at the $(10\overline{1}0)$ surface. There is experimental evidence for the donor activity of O within bulk GaN [10] and total energy calculations show that O sits on a N site [11]. This suggests that oxygen atoms will replace surface N atoms. The added oxygen has an additional electron and because the surface is semiconducting, the additional electron occupies a state near the conduction band. The defect has therefore a high energy. Such a defect would attract acceptors to it and the neutral complex would be stabilized by the emptying of the donor level. 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 [12,13]. There is also evidence from positron annihilation studies for the presence of gallium vacancies in bulk GaN [14]. Consequently, we suppose that the surface oxygen concentration could be sufficiently large, and the oxygen atoms sufficiently mobile, that the three N neighbors of V_{Ga} at the $(10\bar{1}0)$ surface are replaced by O forming the V_{Ga}–$(O_N)_3$ defect.

Here we investigate the energetics and properties of the V_{Ga}–$(O_N)_3$ defect complex at the $(10\bar{1}0)$ surface using an *ab initio* local density–functional (LDF) cluster method, *AIMPRO*, and a self–consistent density–functional tight–binding method *SCC–DFTB*. The latter can be used in large supercells and enables the formation energy of the defects to be found. Details of the methods and their application to the $(10\bar{1}0)$ surface and dislocations in GaN have been given previously [5,15] and will not be repeated here. The two methods gave identical structures to within 5% for bond lengths and 2% for angles.

As an illustrative benchmark for the application of the *SCC–DFTB* method to O in GaN we choose the V_{Ga}–O_N defect complex in its double negative charge state. We find the distance between the vacancy core and the O (N) to be increased by 13.5% (8.9%) in good agreement with the values of 14.9% (9.8%) given by Neugebauer *et al.* [12]. We calculated the energy ΔE for the reaction,

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

in bulk material to be 2.1 eV in good agreement with 1.8 eV [12] and ~ 2.1 eV [16] obtained by plane wave methods. Assuming Ga–rich growth conditions, which are common in many growth techniques, and that O is in equilibrium with Ga_2O_3, corresponding to an upper limit for the O concentration [11], we derive an absolute formation energy of ~ 1.2 eV in n-type material, which is again very close to the plane wave values (~ 1.1 eV in ref. [12] and ~ 0.9 eV in ref. [16]).

We now apply these methods to V_{Ga}–$(O_N)_3$ at the $(10\bar{1}0)$ surface. In the *SCC–DFTB* case the $(10\bar{1}0)$ surface is modeled within a $4{\times}2$ (12.7 Å $\times$ 10.1 Å) unit cell containing 14 monolayers of GaN. Hydrogen was used to saturate the dangling bonds at the bottom of the slab. Atoms in the top ten monolayers were allowed to relax whereas the four bottom monolayers were fixed to preserve bulk symmetry. The clusters used in *AIMPRO* contained 149 atoms.

We find that the energy of a O_N defect in its neutral (positive) charge state is 0.8 eV (0.9 eV) lower at the relaxed $(10\bar{1}0)$ surface than in a bulk like region (all calculations were carried out in the surface cell). This shows that there is a tendency for O to segregate to the surface but is off-set by the configurational entropy encouraging the defect to remain in the bulk. The balance must depend on the details of the surface to volume ratio.

We next consider the V_{Ga}–$(O_N)_3$ defect (see Fig. 1). A similar calculation showed that this defect is also more stable at the surface by 2.2 eV. Furthermore, the defect is electrically inactive with the O atoms passivating the vacancy in the same way as the fully hydrogenated vacancy, VH_4, in Si. Two O neighbors of the surface vacancy are sub-surface and each bonded to three Ga neighbors (Ga–O bond length 1.78 Å to surface Ga, 1.81 Å to second layer Ga and 1.98 Å to third layer Ga atom), but the surface O is bonded to two subsurface Ga atoms at a normal oxygen bridge site (1.77 Å). With a formation energy of 1.7 eV per V_{Ga}–$(O_N)_3$ site (calculated for Ga–rich growth conditions and O in equilibrium with Ga_2O_3) below the defect free $(10\bar{1}0)$ surface, V_{Ga}–$(O_N)_3$ at the $(10\bar{1}0)$ surface is a very stable arrangement (we have also investigated O in a variety of positions at the $(10\bar{1}0)$ surface including O_N, O_{Ga}, neighbouring O_N–O_{Ga} and O as a bridge between the Ga dangling bond and the N lone pair, but find that all of them have higher energies than V_{Ga}–$(O_N)_3$. Furthermore V_{Ga}–$(O_N)_3$ does not encourage overgrowth. Growth 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 an unstable defect $(O_N)_3$ which even under Ga–rich growth conditions is by 1.5 eV higher than V_{Ga}–$(O_N)_3$. At the growth temperature, the oxygen atoms will then drift away diffusing to the new surface.

To explain the formation of nanopipes, we suppose that oxygen atoms constantly diffuse to the $(10\bar{1}0)$ surface. Within the framework of Stranski-Krastanow growth, the internal $(10\bar{1}0)$ surfaces between GaN islands are shrinking along with the spaces between colliding GaN islands (see Fig. 3). Thus the O coverage and density of V_{Ga}–$(O_N)_3$ defects is expected to increase. The maximum concentration of this defect would be reached if 50% (100%) of the first (second) layer N atoms were replaced by O (see Fig. 2). It is, however, likely that far lower concentrations are necessary to stabilize the surface and make further shrinkage of the inter-island spaces 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 has indeed been observed by Liliental–Weber *et al.* [17] who found that as the concentration of oxygen in the material changed by about an order of magnitude the number of nanopipes increased by a factor of ~ 3 and the diameter of the nanopipes changed from (3–10) nm to (6–12) nm. A more detailed prediction of the radii and density of nanopipes depending on the oxygen partial pressure would require thermodynamic equilibrium for the formation of the nanopipes. However, as can be seen in the large distribution of nanopipe radii this is obviously not reached.

It is also necessary to explain why the tubes have $(10\bar{1}0)$ walls. The other low index surface perpendicular to the growth direction which could become impoisoned by O impurities and thus be responsible for the formation of nanopipes is the $(11\bar{2}0)$ surface. Our calculations show that the V_{Ga}–$(O_N)_3$ defect complex is also stable at the stoichiometric $(11\bar{2}0)$ surface. However the formation of V_{Ga}–$(O_N)_3$ at $(11\bar{2}0)$ is not as likely as at $(10\bar{1}0)$ where one O_N emerged to the surface can very easily attract or create a gallium vacancy reducing the Coulomb energy. Already this gallium vacancy oxygen (V_{Ga}–O_N) complex is stable at $(10\bar{1}0)$: O sits two fold coordinated and two N atoms have three bonds. V_{Ga}–O_N will then attract another two O to form a charge neutral V_{Ga}–$(O_N)_3$ complex. This mechanism however does not exist at the $(11\bar{2}0)$ surface where V_{Ga}–O_N at the surface would result in a two–fold coordinated N atom which is a high energy configuration. Indeed our calculations show that the energy of V_{Ga}–O_N at the $(11\bar{2}0)$ surface is by 1.5 eV higher than at the $(10\bar{1}0)$ surface. At the $(11\bar{2}0)$ surface V_{Ga} would only be created by two surface O_N. This is not very likely to happen, since the oxygens are positively charged donors and thus repeal each other. We therefore conclude that although V_{Ga}–$(O_N)_3$ defect complexes are stable at both types of nonpolar GaN surfaces they are not likely to occur at the $(11\bar{2}0)$ surfaces. Moreover

$(11\bar{2}0)$ surfaces are not observed presumably because of their higher absolute surface energy [9].

Finally, we point out that our arguments are still valid if each nanopipe is associated with a screw dislocation. This follows as the walls of the tube with a dislocation are locally equivalent to a $(10\bar{1}0)$ surface which is distorted to form a helix [5]. The presence of oxygen in the nanopipe could be easily checked by energy loss spectroscopy.

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 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 $(10\bar{1}0)$ walls coated with GaO and supports the suggestions of Liliental-Weber *et al.* that nanopipes are linked to the presence of impurities [8].

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FIGURES

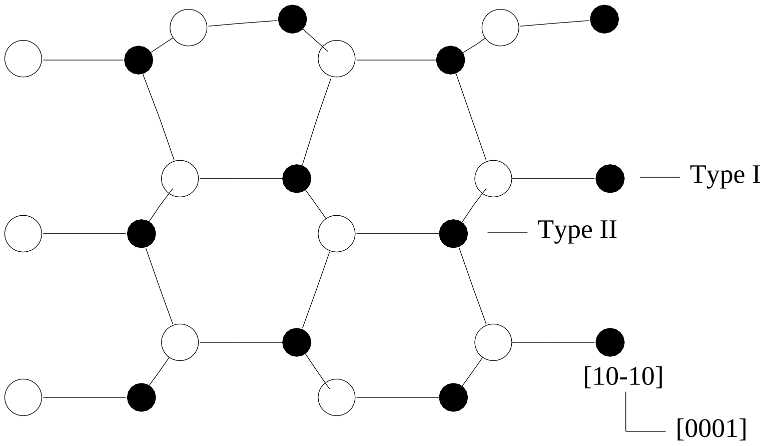

FIG. 1.

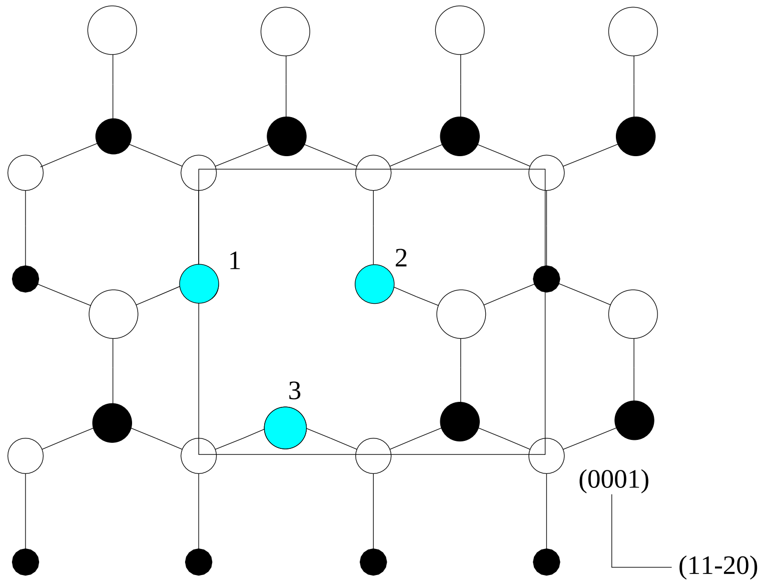

FIG. 2.

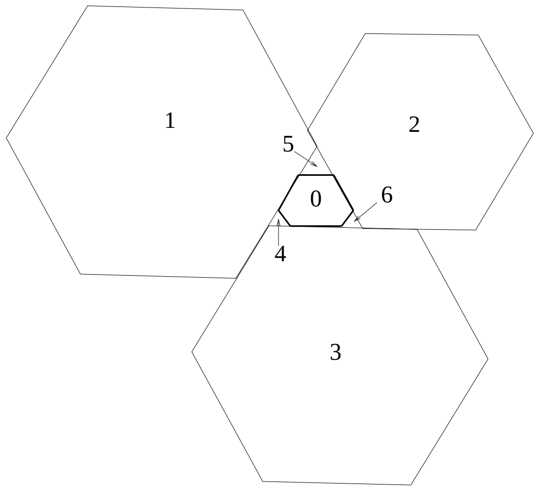

FIG. 3.

Figure I:

Side view along $[11\bar{2}0]$ of the $(10\bar{1}0)$ surface. White (black) circles represent Ga (N) atoms. Type I surfaces have one dangling bond (lone pair) per Ga (N) surface atom. Type II surfaces have two dangling bonds (lone pairs) per Ga (N) surface atom and have therefore high surface energies.

Figure II:

Schematic top view of the V_{Ga}–$(O_N)_3$ defect complex at the $(10\bar{1}0)$ surface of wurtzite GaN. White (black) circles represent Ga (N) atoms and large (small) circles top (second) layer atoms. Atoms 1 and 2 are three–fold coordinated second layer O atoms each with one lone pair, atom 3 is a two–fold coordinated first layer O with two lone pairs.

Figure III:

Schematic view (in [0001]) of the formation of a nanopipe (area No. 0). Three hexagons (No. 1,2,3) are growing together. As the surface to bulk ratio at ledges (No. 4,5,6) is very large, they grow out quickly leaving a nanopipe (area No. 0) with $\{10\bar{1}0\}$ type facets.

REFERENCES

[1] W. Qian, G.S. Rohrer, M. Skowronski, K. Doverspike, L. B. Rowland, and D. K. Gaskill, Appl. Phys. Lett. **67**, 2284 (1995).

[2] W. Qian, M. Skowronski, K. Doverspike, L. B. Rowland, and D. K. Gaskill, J. Cryst. Growth **151** 396, (1995).

[3] P. Vennéguès, B. Beaumont, M. Vaille, and P. Gibart, Appl. Phys. Lett. **70**, 2434 (1997).

[4] F. C. Frank, Acta. Crys. **4**, 497 (1951).

[5] 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).

[6] P. Pirouz, unpublished

[7] D. Cherns, Private Communications

[8] Z. Liliental–Weber, Y. Chen, S. Ruvimov, and J. Washburn, Phys. Rev. Lett. **79**, 2835 (1997).

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

[10] C. Wetzel, T. Susiki, J.W. Ager, E.R. Weber, E.E. Haller, S. Fischer, B.K. Meyer, R.J. Molnar and P. Perlin, Phys. Rev. Lett. **78** 3923 (1997).

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

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

[13] P. Bougulawski, E.L. Briggs, and J. Bernholc, Phys. Rev. B **51** R17255 (1995).

[14] K. Saarinen, T. Laine, S. Kuisma, J. Nissilä, P. Hautojärvi, L. Dobrzynski, J.M. Baranowski, K. Pakula, R. Stepniewski, M. Wojdak, A. Wysmolek, T. Suski, M. Leszcynski, I. Grzegoryy and S. Porowski, Phys. Rev. Lett. **79** 3030 (1997).

[15] M. Elstner, D. Porezag, G. Jungnickel, J. Elsner, M. Haugk, Th. Frauenheim, S. Shuhai and G. Seifert, accepted for publication in PRB 1998.

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

[17] Z. Liliental–Weber, Y. Chen, S. Ruvimov, and J. Washburn, Mat. Science Forum **258–263**, 1659 (1997).