DFT analysis of crystal polarity on graphene surface

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Abstract. We report an *ab-initio* study of the preferred polarity for wurtzite GaN nanostructures on virtual graphene substrates. By means of the density functional theory analysis we show that N-polar nanostructures on graphene are energetically favorable in comparison to Ga-polar. These finding are in agreement with experimentally observed N-polarity of wurtzite GaN nanowires grown on graphene substrate. We believe that the revealed polarity preference is of importance for piezoelectric and optoelectronic device design.

1. Introduction

Gallium nitride (GaN) nanostructures can be employed as active components for a wide range of device applications such as light-emitting diodes [1, 2], solar cells [3–7], photodetectors [8] and piezogenerators [9–11].

GaN nanostructures usually form wurtzite crystal structure which lacks the inversion symmetry of [0001] and [000̅1] directions [12] resulting in a spontaneous polarization along the c-axis (in the [0001] direction). Thus the Ga-polar structures growing in [0001] direction can be distinguished from the N-polar ones growing in [000̅1] direction. The polarity of the growth front is widely known to influence the GaN optical [13] and electronic [14] properties and therefore impacts their use in piezoelectric [10] and light-emitting [15] devices.
While the nanosized GaN crystals can be formed epitaxially on a number of different substrates, the growth on virtual graphene substrate is promising in terms of the so-called van-der-Waals epitaxy. In this case the nanostructure can be lifted off the growth substrate and transferred to any other arbitrary substrate. However, unlike the growth on conventional substrates such as silicon or sapphire, the polarity of GaN grown on graphene is not well-explored. In this work we employ the density functional theory (DFT) analysis to study the polar properties of GaN clusters forming on graphene.

2. Results and discussion

We perform the DFT calculations to determine the most energetically preferable geometry of the GaN nanocluster on graphene. Such a clusters can represent the nucleus of GaN nanoisland or nanowire. To reproduce the hexagonal symmetry of the wurtzite structure at least ten gallium and ten nitrogen atoms should be considered. In addition sixty more carbon atoms form the monolayer graphene lattice.

This model system system allows eight possible geometric configurations of GaN nanocluster: four Ga-polar and four N-polar. However, only two out of eight configurations are found to be stable during the energy optimization [16] within DFT calculations in the plane-wave basis set for projector augmented-wave method implemented in GPAW package [17]. The calculations was carried out using the Perdew–Burke–Ernzerhof generalized gradient approximation for exchange-correlation functional, with the plane wave energy cutoff set to 450 eV and $k$-space sampling in $4\times4\times4$ Monkhorst-Pack grid. To reduce computation time, the graphene atoms were fixed the during optimisation procedure.

The evolution of the two stable configurations, initially one Ga-polar and one N-polar, is illustrated in Figure 1 (a). We observe the initially Ga-polar cluster to change the Ga-N dipole orientation during the optimization procedure. Meanwhile, the initially N-polar nanocluster adjusts shape while keeping the initial arrangement of the atomic planes and the Ga-N dipole orientation. Thus, both stable configurations evolve to N-polar geometry corresponding to minimal cluster energy.

![Figure 1](image.png)

**Figure 1.** Snapshots of GaN NCs geometries before and after optimisation (a) for Ga-polar NC, (b) for N-polar NC. The $\Delta E$ show the energy difference between initial and final states. The energy difference between two systems in final states is less 0.5 eV. (c) 25° tilted SEM image of the system after the KOH etching.
Our model results are consistent with the experimentally observed preference of N-polarity in the growth of GaN nanowires on graphene/SiO\textsubscript{x}/Si substrates. The details of GaN nanowire epitaxial growth can be found in our previous works [18,19].

Figure 1 (c) shows a scanning electron microscopy (SEM) image of the grown GaN NWs on graphene and treated by KOH attack. Treatment in KOH solution leads to sharpening of NW tips due to crystal plane selective etching, which is a characteristic property of the N-polar structures [20]. The subsequent SEM imaging reveals that all GaN NWs grown on graphene possess N-polarity.

![Figure 1](image1)

**Figure 2.** Snapshots of the N-polar GaN nanocluster (a) before optimisation procedure, (c) after optimisation procedure, (b) dependence of system potential energy on optimisation step.

Figure 2 shows the influence of all atom, including the graphene ones, optimisation on the final geometry of the system. For that we took the optimised geometry of N-polar GaN NC and include the graphene atoms into optimisation procedure. It is seen that the total energy of the system drops by ≈ 200 meV and the graphene layer sags under the NC. But, more importantly, there was no significant changes in the NC geometry.

3. Conclusions
The presented DFT study have shown that N-polar GaN structures on graphene substrates are energetically preferable to Ga-polar ones. Among different possible configurations of Ga and N atoms in the cluster only the N-polar one is stable while the initially Ga-polar structure demonstrates the change of polarity during the ab-initio optimization. The DFT modeling results are consistent with the experimental observations of exclusive N-polarity of GaN NWs grown on graphene layer on top of silicon substrate.

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simulations. The molecular structures in this article were rendered using Ovito software package [21].

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