Computing Equilibrium Shapes of Wurtzite Crystals: The Example of GaN

Hong Li,1, 2, ∗ Lutz Geelhaar,2 Henning Riechert,2 and Claudia Draxl1

1Institut für Physik und IRIS Adlershof, Humboldt-Universität zu Berlin, Zum Großen Windkanal 6, 12489 Berlin, Germany
2Paul-Drude-Institut für Festkörperelektronik, Hausvogteiplatz 5-7, 10117 Berlin, Germany

Crystal morphologies are important for the design and functionality of devices based on low-dimensional nanomaterials. The equilibrium crystal shape (ECS) is a key quantity in this context. It is determined by surface energies, which are hard to access experimentally but can generally be well predicted by first-principles methods. Unfortunately, this is not necessarily so for polar and semipolar surfaces of wurtzite crystals. By extending the concept of Wulff construction, we demonstrate that the ECSs can nevertheless be obtained for this class of materials. For the example of GaN, we identify different crystal shapes depending on the chemical potential, shedding light on experimentally observed GaN nanostructures.

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Low-dimensional semiconductor nanostructures have attracted lots of interest in the past decades, largely due to their applications in low-energy consumption and energy-harvesting devices [1, 2]. Owing to surface effects, the performance of such devices strongly depends on the nanocrystal morphology. To achieve comprehensive understanding and control the preferred growth morphology, the natural shape of a material resulting from its crystallographic anisotropy is inevitable to know. Ab initio theory can generally provide more insight into this complicated issue through the calculation of surface energies since, according to Wulff’s theorem [3], the equilibrium crystal shape (ECS) of a solid can be constructed by the mere knowledge of surface energies of various crystal planes. For a crystalline solid, the surface energy \( \gamma \) is defined as the excess free energy required to create one unit of surface area \( A \) [4]

\[
\gamma = \frac{1}{A} \left[ G - \sum_i N_i \mu_i \right].
\] (1)

\( G \) represents the Gibbs free energy of the system that, neglecting temperature and pressure, is replaced by the total energy. The chemical potential \( \mu_i \) is the free energy per atom in the system for species \( i \), and \( N_i \) denotes the number of atoms of this species. In a bulk material, the total chemical potential is known from the corresponding total energy \( E_{\text{bulk}} = \sum n_i \mu_i \). Hence, the surface energy of a nonpolar plane can be extracted from density-functional-theory (DFT) results for a slab, that contains two identical surfaces well separated from each other. For some polar and semipolar planes, however, individual surface energies are difficult to access, because different facets may appear at the two surfaces of the slab. To overcome this problem, a method has been proposed [5] that involves two surface types on three side faces of a triangular wedge. This approach is, however, not applicable to all surfaces and crystal structures, like polar surfaces in wurtzite crystals [6]. As a consequence, not every individual surface energy of a wurtzite crystal can be computed, and, hence, the construction of the ECS seemed impossible. Recently, neglecting the different layer-stacking sequence, the surface energy of the polar \( c \) plane was estimated from the zincblende (111) plane [7]. In this work, we show that such an approximation is not required to unambiguously determine the ECS. We introduce a generalization of the Wulff construction based on combinations of surface energies to show how the ECS for the class of wurtzite materials can be obtained. We demonstrate this principle taking GaN as a technologically important example.

The wide band-gap semiconductor GaN is a key material in today’s white light-emitting diodes for general illumination, blue lasers as well as high-power and high-frequency electronics [8]. GaN readily grows in the form of nanowires (NWs) in molecular beam epitaxy (MBE) [9, 10] and metal-organic chemical vapor deposition (MOCVD) [11, 12]. However, different shapes are observed depending on growth temperature, pressure, and chemical environment [13–17]. Our study leads to new understanding of these GaN crystal shapes under various growth conditions.

We performed DFT calculations in the local-density-approximation using the projector-augmented-wave method [18] as implemented in the Vienna Ab Initio Simulation Package (VASP) [19, 20]. The plane-wave energy cutoff was set to 400 eV, and a \( 8 \times 8 \times 6 \) Monkhorst-Pack [21] k-mesh was chosen for the Brillouin zone sampling in the primitive wurtzite cell. For slabs and wedges, the k-mesh was scaled accordingly with respect to the cell size. The total energy was converged within \( 10^{-5} \) eV/cell. Individual surface energies as well as combinations thereof were carefully converged with respect to slab thickness, wedge size, and vacuum separation. For asymmetric slabs, a dipole correction [22] was applied. Surface reconstructions were not taken into account. The facets of the wedges were saturated by fractionally-charged H atoms, i.e., with an electron/proton charge of 0.75e and 1.25e for each surface N and Ga atom, respectively [23]. These vertical H-N and H-Ga bonds were relaxed by additional slab calculations.

The crystal planes considered here were chosen on the basis of experimental data and include the nonpolar \( m \) plane (1T00) and \( a \) plane (1120), the polar \( c \) planes (0001) and...
TABLE I. Average surface energies (in meV/Å²) of two opposite surfaces obtained from differently oriented slabs. Corresponding surface terminations are described in the text.

| slab       | [1100] | [1120] | [0001] | [1122] | [1101] | [1102] |
|------------|--------|--------|--------|--------|--------|--------|
| γₙᵣ       | 124    | 132    | 209    | 223    | 249    | 208    |

(0001), as well as the semipolar planes (1122), (1122), (1101), (1101), (1102), and (1102). Since for polar and semipolar planes the surface can have different terminations, below we label a surface by its plane indices together with a subscript of the terminating layer or bilayer.

We construct six differently oriented slabs, i.e., along [1010], [1120], [0001], [1122], [1101], and [1102], and calculate the surface energies according to Eq. (1). For the a plane and m plane, individual surface energies are directly determined, because the two surfaces of the slab are identical. For the other slabs only the sum (average) of the surface energies of the two sides can be obtained. Depending on the two surface terminations, these slabs can be stoichiometric or nonstoichiometric, where for the former, the sum of surface energies is independent of the chemical potential. Having considered two surface terminations for either side, we now determine the energetically most favorable combinations. For the [0001] slab, γₙᵣ of (0001)Ga and (0001)N is lower than that of (0001)N and (0001)Ga. For the [1122] slab, the combination of (1122)Ga and (1122)N is more stable than that of (1122)N and (1122)Ga. Further, we identify (1101)2N and (1101)2Ga to be favorable over (1101)2Ga and (1101)2N. And surface terminations of (1102)GaN and (1102)GaN exhibit lower γᵣ than (1102)Ga combined with (1102)N. The respective minimum average surface energies are summarized in Table I together with the individual values for the a and m planes. In agreement with previous DFT results [24], we find the m plane more stable than the a plane, with an energy difference of 8 meV/Å². The average surface energies of the polar and semipolar planes are higher than those of nonpolar planes, indicating the preferential growth mainly along the c axis, as always observed for GaN nanowires.

To construct the ECS, we need surface energies in order to solve the equation,

\[ r(h) = \min_{\mathbf{m}} \left( \frac{\gamma(\mathbf{m})}{\mathbf{m} \cdot \mathbf{h}} \right), \quad (2) \]

where \( r(h) \) denotes the radius of the crystal shape along a given vector \( \mathbf{h} \), and \( \gamma(\mathbf{m}) \) is the surface energy of a plane with normal vector \( \mathbf{m} \). Since individual surface energies are not accessible for wurtzite crystals, straightforward solution of Eq. (2) is not possible. However, an alternative geometrical route for determining the ECS can be accomplished using suitable surface-energy combinations. To illustrate this idea, Fig. 1 depicts a two-dimensional (2D) schematic for a generalized Wulff construction. With \( \gamma_{0001} + \gamma_{0001} \) the distance MN between these two planes is fixed, but not their position with respect to the origin O. This uncertainty, however, does not influence the crystal shape, because the surface-energy combinations actually fix its inner envelope. For instance, \( \Delta \gamma_1 = \frac{\gamma_{102}}{\cos \theta_1} - \gamma_{0001} \), corresponding to the distance LM, provides the difference in hypothetical crystal radii of the (102) plane, OL, and the (0001) plane, OM, along the [0001] direction. (Hypothetical refers to the fact that the individual surface energies are not known.) Knowing LM and the dihedral angle \( \theta_1 \) given by the lattice parameter, the crossing point \( P_1 \) of these two planes is determined. Similarly, \( \Delta \gamma_2 = \frac{\gamma_{101}}{\cos \theta_2} - \gamma_{0001} \) fixes the length HM and, thus, together with \( \theta_2 \) we know the crossing point \( P_2 \). Since OQ can be calculated directly, the crossing point P is clear. Overall, despite the vertical coordinates of these points being unknown, a quarter of the crystal shape, i.e., the shaded area in Fig. 1 is fully determined. Analogously, the three other quarters of the 2D crystal shape can be constructed. Varying individual surface energies will only shift the entire ECS along the c axis by a constant. In fact, it had been shown already in 1975 [25] for 10 point groups that such a constant prevents the determination of certain surface energies, but not necessarily the determination of the ECS. However, up to date no way of constructing an ECS for such cases has been demonstrated.

Having achieved this goal as illustrated above, we need to show now that such surface-energy combination \( \Delta \gamma \) can be indeed calculated for each semipolar plane. To this end, we employ combinations of slab and wedge calculations. Firstly, we construct different types of wedges, infinitely long 1D structures with triangular cross sections, that are depicted in Fig. 2. Each of them exhibits three facets but only two different types of surfaces. The size of the wedge is quantified by the number of atoms \( l \) at the bottom edge of the triangle. By varying the wedge size, the ridge contribu-
The energy differences of the two other [1120] oriented wedges in Fig. 2(b) and (c) are calculated by

\[ \delta E_b^{un} = \frac{(E_b^{l=21} - E_b^{l=17} - 74E_{\text{bulk}} - 4\mu_N)}{4} \]

(4)

\[ \delta E_c^{un} = \frac{(E_c^{l=20} - E_c^{l=16} - 36E_{\text{bulk}} - 2\mu_N)}{2} \]

(5)

Likewise, exchanging Ga and N positions in the wedges, we arrive at expressions for the opposite crystal planes. No numerical results are given here, since they depend on the chemical potential. We note, however, that the energy differences \( \delta E \) have been converged within 0.1 eV with respect to the wedge size, corresponding to an accuracy in surface energy within about 10 meV/Å².

In a next step, we construct slabs containing the semipolar surfaces that have been considered before in the wedges and calculate the corresponding surface-energy sums without geometry relaxation. For instance, from the [1122] oriented slab, according to Eq. (1), we obtain \( \sigma_{1122}^{un} + \sigma_{1122}^{1122} \). Combining it with Eq. (3), results in \( \sigma_{1122}^{un} - 2\sigma_{0001}^{1122} \). Accordingly, \( \sigma_{1122}^{un} - 2\sigma_{0001}^{1122} \) is derived. Applying the same strategy to the other two types of wedges, we obtain the relative energy of an unrelaxed semipolar facet with respect to its neighboring unrelaxed polar facet. Since these calculations are intermediate steps only, surface relaxation and reconstruction are ignored intentionally.

Finally, we show how to determine the decisive surface-energy combinations by taking into account surface relaxations. Each of them is obtained from two additional slab calculations, where one (clean) surface is relaxed while keeping the reference surface at the other side fixed and saturated with H. Table II lists all the surface-energy combinations calculated from the wedges only (I) or in combination with the slabs (II and III). Obviously, from combinations I and II, combinations III are derived. Dividing the latter by...
the respective semipolar surface-unitcell area, uniquely fixes the ECS. A sketch of the overall procedure together with one representative example can be found in the Supplementary Material.

The resulting relative energies $\Delta \gamma$ are plotted in Figs. 3(a) and (b). Typically, the chemical potential of nitrogen $\mu_N$ can vary from Ga-rich to N-rich conditions, $E_{\text{GaN}} - E_{\text{Ga}} \leq \mu_N \leq E_{\text{N}_2}$, where $E_{\text{GaN}}$ and $E_{\text{Ga}}$ represent the total energies of wurtzite GaN and bulk Ga, respectively, and $E_{\text{N}_2}$ is the total energy (per atom) of the $N_2$ molecule. In the figure, this range is extended by 2 eV on both sides to mimic experimental temperature and pressure conditions. We find in Fig. 3(a) that the (0001)$_N$ termination has higher surface energy than the (0001)$_{Ga}$ termination over the whole considered range of $\Delta \mu_N$. $\Delta \gamma$ of the (1101)$_{2Ga}$ surface becomes negative when $\Delta \mu_N$ is low. On the other hand, $\Delta \gamma$ of the (1102)$_{GaN}$ surface becomes negative when $\Delta \mu_N$ is high. Therefore, the (1101)$_{2Ga}$ and (1102)$_{GaN}$ surfaces dominate the Wulff construction in these two extreme cases. For an intermediate range of $\Delta \mu_N$, the (0001)$_{Ga}$ surface has the lowest energy, thus this surface remains at the top of the crystal. On the bottom side, as shown in Fig. 3(b), the situation is different. The (0001)$_{Ga}$ surface is more stable than the semipolar surfaces, and only for higher $\Delta \mu_N$ (0001)$_N$ becomes more favorable. This means that the crystal is either terminated by the (0001)$_{Ga}$ or (0001)$_N$ facet under various $\Delta \mu_N$ conditions.

Fig. 3(c) shows the 3D Wulff crystals constructed from the above results. We summarize the major features: (i) The GaN crystal, in general, exhibits a rod-like shape along [0001] under various conditions. (ii) The shapes on the top and bottom side are changing according to the chemical potential. Under extremely Ga-rich conditions, the crystal forms a complete pyramid consisting of {1101} planes at the top. When $\Delta \mu_N$ increases to a higher value, the crystal adopts the shape of a truncated pyramid, and eventually turns into another pyramid formed by {1102} facets. At the bottom side, the flat (0001) surface turns into a polyhedral shape consisting of (0001), {1122}, and {1101} planes, and further formed by {1102} and {1100} planes only. Finally, the flat (0001) plane appears again. (iii) The side wall consists of both nonpolar facets, namely the $m$ plane and the $a$ plane. These findings complement those of Lymperakis and Neugebauer [26], who have shown that the coexistence of these facets facilitates two diffusion channels for Ga atoms. When Ga atoms arrive at the $m$ plane (indicated by the blue color), lateral diffusion is favorable while for Ga atoms at the $a$ planes (green color), vertical diffusion along the $c$ axis takes place. As a matter of fact, Ga atoms accumulate at the top of the crystal and axial growth continues. The appearance of two nonpolar planes on the side walls also agrees with recent experimental studies [16, 27] that nanocolumns (NCs) and NWs indeed do not exhibit atomically sharp corners.

Let us finally recall the variety of experimentally achieved crystal morphologies: Selective-area MOCVD growth [13] exhibited convex {1101} and concave {1122} surfaces. In contrast, Jindal [14] observed in MOCVD growth a complete hexagonal pyramid on the (0001) plane as its equilibrium shape, and truncated hexagonal pyramids out of equilibrium, while the crystal grown on the (1120) and (1100) planes showed {1101} facets along the [0001] direction and a (0001) facet on the opposite side. Depending on the temperature and pressure in hydride vapor phase epitaxy.

![Fig. 3.](image)

FIG. 3. (color) The relative energy $\Delta \gamma$ versus chemical potential plots and GaN crystal shapes. (a) The relative energy $\Delta \gamma$ plot along the [0001] direction. (b) The relative energy $\Delta \gamma$ plot along the [0001] direction. (c) GaN crystals under thermodynamic equilibrium conditions. The shape varies continuously from Ga-rich conditions (left) to N-rich conditions (right). The underlying label - pyramid I, truncated pyramid, and pyramid II - refers to the top shape.
(HVPE) [15], the truncation of the pyramidal shape was confirmed, continuously varying along the [0001] direction. More recently, semipolar \{102\} facets on top of GaN NCs were reported from selective-area MBE growth [16]. Considering our theoretical results, these observations are not controversial. In fact, most of the observed crystal morphologies are consistent with our computed ECSs. Particularly, the crystal shape under N-rich conditions is fully consistent with the different morphologies of GaN NWs [12, 28, 29], where pyramid or truncated pyramid shapes are observed in the case of Ga-polar NWs, and the flat (000T) facet dominates the top in the case of N-polar NWs. At the same time, the aspect ratio of experimental NWs can be much larger than seen in these ECSs. This difference implies that kinetic effects also play an important role in NW growth.

To summarize, we have demonstrated a generalization of Wulff construction to determine equilibrium crystal shapes for wurtzite crystals. Although the individual surface energies for semipolar and polar surfaces are not accessible, the crystal shape can still be obtained, \textit{e.g.}, from DFT calculations. For each semipolar plane, the relative energy with respect to its neighboring polar plane can be unambiguously computed as a function of the chemical potential. This energy difference, corresponding to the crystal radius along the polar axis, is the important quantity that governs the crystal shape. We have exemplified our approach with the case of wurzite GaN. Taking into account several bulk-truncated ECSs have been constructed. We have found that the crystal exhibits a rod-like shape along the polar \textit{c} axis, with top and bottom geometries depending on the chemical potential, while the side walls are formed by both types of nonpolar surfaces. Our results can well explain the experimentally observed NW shapes. Beyond that, it opens a perspective to gain insight into morphologies of the entire class of wurtzite materials.

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\* hong.li@physik.hu-berlin.de

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The overall scheme of our calculations is sketched in Fig. S1, that involves five steps: (1) The most stable surface terminations of one semipolar plane and one polar plane are adopted to build the 1D wedge structures (top left). This allows us to determine the sum of surface energies of a semipolar surface and a polar surface. (2) Using a 2D slab, the sum of two surface energies is obtained for different slab orientations (bottom left). (3) Combining the sum of surface energies obtained from the wedge (I) with the sum of surface energies obtained from the slab, combination II is derived (upper middle part). (4) Additional calculations are carried out with the slab approach. However, this time, one of the two surfaces of a slab is relaxed while the opposite surface is kept fixed and H-saturated as in previous cases of slabs and wedges. That way, the sum of surface energies of a relaxed surface and an unrelaxed surface is obtained (middle bottom part). (5) Finally, these surface-energy sums are added to combinations II to achieve combinations of type III. As explained in the main paper, such surface energy relations (surface-energy combination III divided by surface unit cell area) actually determine the equilibrium crystal shape.

Fig. S2 illustrates a particular example, involving three types of calculations for determining the surface-energy combination \( \sigma_{1T02}^{\text{un}} - 2\sigma_{0001}^{\text{un}} \) for the case of the (1T02)\text{GaN} surface and the (0001)\text{Ga} surface. Results for various other crystal planes as well as different surface configurations can be calculated in the same way.