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Understanding the cubic AlN growth plane from first principles

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ABSTRACT

The structure of clean and reconstructed cubic AlN (0 0 1) surfaces has been investigated from first principles. In the nitrogen rich part of the phase diagram, a nitrogen termination has been found to be favored. Under aluminum-rich conditions, a contracted adlayer of Al-atoms on top of an Al-termination is favored.

Aluminum nitride (AlN) has been investigated for a couple of decades already, however, mainly from a technological point of view. While its mechanical and thermodynamic properties made AlN an interesting high performance ceramic material, technology is now focussing more and more on its electronic and optical properties. Mainly due to new experimental insights about its potential use in III–V heterostructures, the optical properties have been investigated in a recent paper [2]. Similar to gallium nitride (GaN), AlN exists both in wurtzite and zinc blende (zb) phase with the latter being less stable, i.e. metastable, but having the advantage of not having a polarization electrical field in the (0 0 1) growth direction [3,4]. Heterostructures built up of zinc blende GaN and AlN or AlGaN exhibit quantum well structures with high emission efficiencies [3]. For building such nanoscale devices, the interface between the materials is of substantial importance, since incorporated defects would ruin the device performance. Smooth surfaces allow for obtaining a nearly perfect interface. It is, therefore, important to find growth modes which yield smooth surfaces, most suitably atomically flat. Although zb-AlN is a metastable phase, it has only recently become possible by plasma assisted molecular beam epitaxy to reduce the usual hexagonal inclusions [5] to a minimum and grow AlN layers with a surface roughness of 0.2 nm RMS [4]. In order to understand this growth mechanism and possibly improve it by adjusting the parameters of the growth conditions, we have calculated surface structures of zb-AlN as they can appear during growth. So far, only few publications deal with detailed atomistic investigations of the properties of clean AlN surfaces [1], mainly focussing on a comparison of different nitrides. However, nothing is known about non-ideal surfaces of zb-AlN. In the following, we present to our knowledge the first ab initio-study on the energetics of the zb-AlN (0 0 1) surface.

Surface structures have been obtained by performing first principles density functional theory (DFT) calculations with the Vienna Ab Initio Simulation Package (VASP) [8]. The PW91 functional [10] was used to model the electron exchange and correlation interaction within the generalized gradient approximation (GGA). The electron–ion interaction was described by the projector-augmented wave (PAW) method [9]. A consistent k-point sampling was chosen, ranging from $(6\times6\times1)$ for the surface structures with (1×1) periodicity to $(2\times1\times1)$ for the largest reconstruction. An energy cut-off of 300 eV has been found to be sufficient. Due to the periodic boundary conditions employed, surfaces were modelled in slabs of nine monolayers AlN material separated by 25 Å vacuum and saturated at the bottom with pseudohydrogen.

The surface energies in the phase diagram 1 have been calculated relative to the clean Al-terminated surface as a reference structure [11]:

$$\begin{aligned}\Delta\gamma &= \gamma_{struc}-\gamma_{ref}\\ &= G_{slab}-G^{0}_{slab}-\Delta n_N G^{AlN}_{bulk}\\ &\quad +(\Delta n_N-\Delta n_{Al})\mu_{Al}\end{aligned} \tag{1}$$

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where

$$\Delta n_{Al} = n_{Al}^{slab} - n_{Al}^{slab,0} \quad (2)$$

In this expression, G_{slab} denotes the free energy of the structure under investigation with reconstruction and/or defect, respectively, and fully relaxed. G_{slab}^{0} denotes the free energy of the ideal slab, the remaining terms account for the different number of nitrogen and aluminum atoms in the defective and the ideal slab.

In thermodynamic equilibrium, the chemical potentials of Al and N are connected via the condition

$$\mu_{AlN}^{bulk} = \mu_{Al} + \mu_{N}, \quad (3)$$

such that one of these quantities can be eliminated. In accordance with experimental papers, we chose μ_{Al} as running variable. The chemical potential of Al can vary between the energy of its most stable phase, i.e. $\mu_{Al}^{fcc-bulk}$, and zero.

Fig. 1 shows the resulting phase diagram for the most stable surface structures relative to the clean ideal Al-terminated surface. The adsorption of nitrogen atoms in low coverage, i.e. one eighth of the available sites, has been calculated to be energetically possible over a large range of the chemical potential of aluminum (green dashed line). The same holds for the adsorption of Al-atoms in the respective Al-coverage (blue dashed line). In both cases, the adatoms prefer to adsorb in their usual crystal sites.

Offering more of the one atomic species, i.e. either more nitrogen atoms or more aluminum atoms, leads us to higher coverages of this one respective component of AlN. Offering more nitrogen, the surface energy is lowered for each further adatom until a fully nitrogen covered surface has been reached. In the nitrogen rich regime, this surface is the lowest energy surface. Offering, instead, only Al-atoms to the surface, the energy is lowered similarly until a full coverage with Al is reached, resulting in an Al double layer on top of the surface.

However, there are more stable surface terminations to be found in the aluminum rich regime. In close analogy to the recently found behavior of cubic GaN surfaces [7], we started to employ the concept of contracted aluminum adlayers on top of the growth surface. As a starting point, we followed the suggestions by Neugebauer and coworkers [6] and chose a pure honeycomb-type Al-layer which we put atop the clean AlN surface. For a freestanding model of this structure, the total energy has been calculated lowest for an interatomic distance of 2.6 Å and a next nearest neighbor distance of 4.4 Å. This latter distance makes it fit ideally on top of the AlN surface which has a lattice constant of 4.4 Å. In the direction perpendicular to this ideally fitting, some mismatch occurs. In our periodic boundary approach, this mismatch has been minimized by choosing the appropriate ratio between the number of surface and adlayer unit cells. The best fitting is obtained for ratio of 7:6, i.e. seven surface unit cells of AlN topped by six unit cells of the flat honeycomb Al-lattice. The overall mismatch then remains 0.28 Å.

Fig. 2(a) shows a ball and stick model of this structure. For better visibility, two unit cells are shown along the shorter direction. Relaxation destroys the honeycomb structure of the adlayer. Fig. 2(b) shows a top and side view of the resulting structure. In some regions, the remainders of the honeycombs can be seen. The sideview reveals that in these regions, the adlayer becomes buckled and does not bind to the substrate Al atoms.

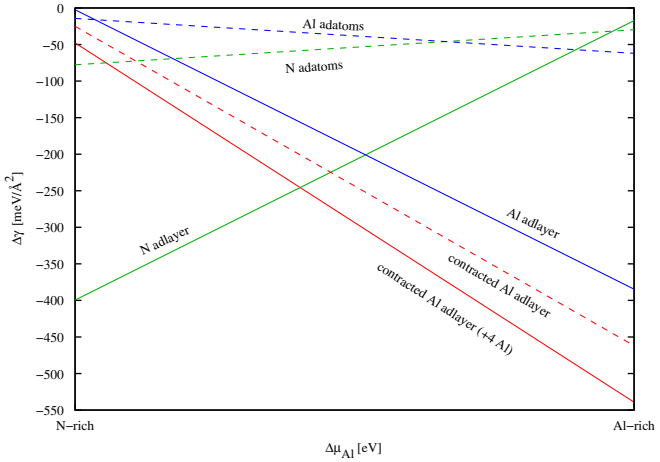

Fig. 1. (color online) Phase diagram of the most stable surfaces. Being the growth surface, the clean ideal Al-terminated surface has been chosen as reference structure. Surface energies $\Delta\gamma$ (meV/Å^2) are plotted via the chemical potential μ_{Al} of aluminum.

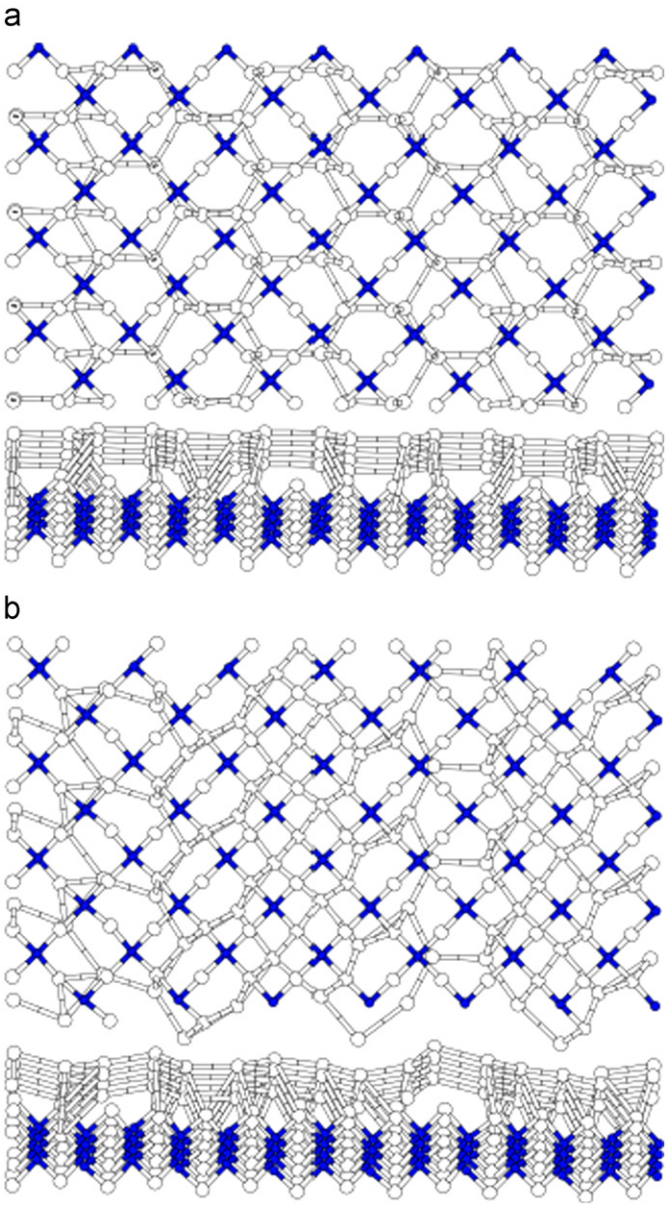

Fig. 2. Top and side views of (a) the ideal honeycomb Al-adlayer and (b) the same structure after relaxation. Nitrogen atoms are drawn blue, Al atoms white. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

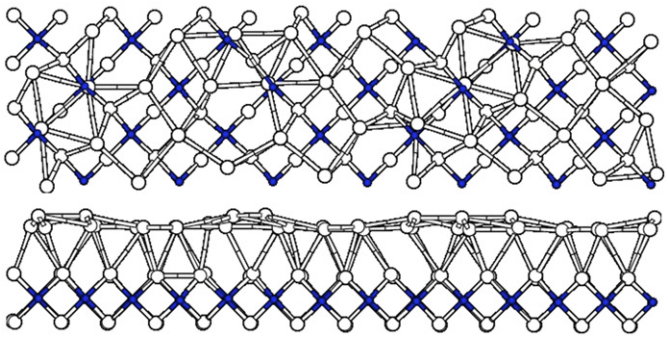

Fig. 3. Top and side views of the Al-adlayer obtained by relaxing the ideal honeycomb and adding four more Al-atoms. Nitrogen atoms are drawn blue, Al atoms white. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Bonding to the substrate appears in the regions of larger reordering in between.

The average height of the adlayer is sited above the Al-termination of the substrate is 2.26 Å. However, it exhibits a strong buckling. While some of the adlayer atoms are as close as 2 Å, others are as far as 2.94 Å away from the substrate measured along the surface normal.

Al–Al bond lengths vary between 2.5 and 2.9 Å within the adlayer, bonds to the substrate have typical lengths of 2.6 Å. We optimized this structure energetically by modifying the number of adlayer atoms in order to obtain a surface that is more stable and has a smaller roughness than this one. Like this, the Al–Al distances both within the adlayer and between adlayer and substrate might get more similar to each other and closer to the Al–Al bondlength in aluminum bulk. For the Al bulk fcc-crystal, DFT calculations yield a bond length of 2.86 Å. We calculated several structures with atoms systematically removed or added to this adlayer. Removing Al-atoms from the adlayer did not lead to stable reconstructions on the surface. Upon adding more Al-atoms to those regions of the adlayer, where the initial honeycomb lattice is rather open, the surface energy of the (2×7) unit cell decreases by approximately 18 meV/Å^2 for each additional Al atom, until a stability maximum with four extra Al-atoms has been reached. The structure (cad4) obtained after relaxation of this construction is shown in Fig. 3. A comparison of the heights of the Al-adatoms above the clean surface termination reveals the flatness which is considerably improved compared to the contracted adlayer discussed above. The buckling or roughness of the surface has been calculated to about 0.2 Å. Furthermore, the adlayer as a whole has come closer to the clean surface, i.e. the average distance is now 2.4 Å.

Fig. 4 shows the density of states (DOS) that has been calculated for this adlayer structure (cad4, lefthand side of the plot) in comparison with the DOS for bulk zb-AlN. The plot reveals clearly the effect of the surface and the additional Al-adatom layer, i.e. the energy gap present in the bulk-DOS on the right is filled with additional, partly occupied levels which are induced by the additional Al-atoms. With its comparably large unit cell, the structure as shown in Fig. 3 gives a rather disordered impression. The local order might only be induced to the structure by the use of periodic boundary conditions. Fig. 5 shows a calculated STM-image (constant current, voltage: 2 eV), for better visibility of two unit cells in vertical direction. With the dark spots located at the more elevated atoms of the adlayer, the local order comes out more clearly than in the ball-and-stick model. Although having calculated this structure to be stable over a wide range of the chemical potential of aluminum, we speculate that the use of larger supercells, instead, might result in even more energetically

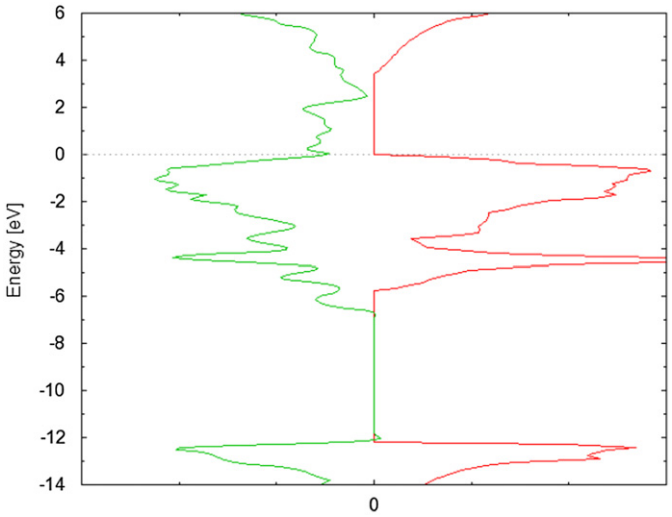

Fig. 4. Density of states (DOS) for bulk zb-AlN (right) and the contracted adlayer (cad4) (left). The Fermi level has been set to zero.

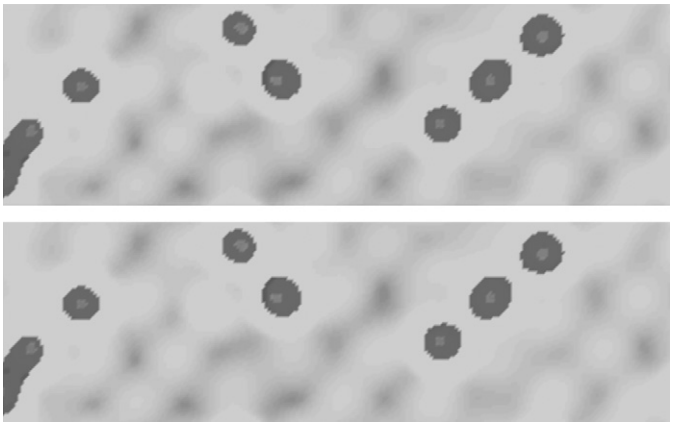

Fig. 5. Simulated STM-image of the most stable Al-adlayer for $V=2$ eV.

favorable and maybe even smoother metallic adlayers. One might even think of a completely disordered, amorphous Al-monolayer similar to the theoretical predictions for Ga-rich GaN [6,7]. In this respect, we present the structure that we found as an optimum for the given setup and for limitations of calculation.

In summary, we performed first principles density functional theory calculations in order to get some insight into the various terminations and reconstructions of zb-AlN (0 0 1) surfaces. Over a wide range of merely nitrogen rich conditions, an unreconstructed nitrogen termination has been found to be most stable. Under more Al-rich conditions, a contracted aluminum adlayer on top of an Al-terminated substrate becomes the most stable structure. This adlayer has been found to be metallic and relatively smooth. The change in stability upon changing the chemical potential of Al may be used for conducting layer by layer growth in order to obtain atomically flat surfaces.

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