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GaN/$LiNbO_3$ (0 0 0 1) interface formation calculated from first-principles

Simone Sanna*, Wolf Gero Schmidt

Lehrstuhl für Theoretische Physik, Universität Paderborn, 33095 Paderborn, Germany

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ABSTRACT

The stable adsorption sites for both Ga and N ions on the ideal and on the reconstructed $LiNbO_3$ (0 0 0 1) surface are determined by means of first-principle total energy calculations. A single N layer is found to be more strongly bound to the substrate than a single Ga layer. The adsorption of a GaN monolayer on the polar substrate within different orientations is then modeled. On the basis of our results, we propose a microscopic model for the GaN/$LiNbO_3$ interface. The GaN and $LiNbO_3$ (0 0 0 1) planes are parallel, but rotated by 30° each other, with in-plane epitaxial relationship $[1\,0\,\bar{1}\,0]_{GaN} \| [1\,1\,\bar{2}\,0]_{LiNbO3}$. In this way the (0 0 0 1) plane lattice mismatch between GaN and $LiNbO_3$ is minimal and equal to 6.9% of the GaN lattice constant. The adsorbed GaN and the underlying $LiNbO_3$ substrate have parallel *c*-axes.

1. Introduction

Gallium Nitride (GaN) and its related compounds (III-Nitrides) have been studied intensively from the beginning of the 90s because of their excellent optical and electrical properties. Most commercial light emitting diodes, laser diodes, and high power/high frequencies electronic devices are currently GaN-based [1,2]. However, the lack of a native substrate for the III-nitrides growth represents a drawback for many applications. It is well known that epitaxially grown GaN is affected by an high density of lattice defects. This is due to the considerable lattice mismatch (around 16%) between GaN and α-Al_2O_3, the most widely used substrate [3]. To overcome this problem many different substrates have been suggested. Among these, ferroelectrics like $LiNbO_3$ (LN) and $LiTaO_3$ (LT) have attracted much attention because of their relatively small lattice mismatch with respect to GaN and their outstanding cost–performance ratio [4–6]. The (0 0 0 1) plane of LN has, just like α-Al_2O_3, hexagonal symmetry, but provides a nominal lattice mismatch of only 6.8% with the GaN (0 0 0 1) plane, which results in a better GaN crystal quality [5]. The key advantage of this substrate is, however, the possibility to use the LN ferroelectricity to control the GaN growth, allowing new polarization engineered structures. As an example, the recently demonstrated monolithic integration of GaN electronic devices with LN waveguides, allows for the creation of sophisticated signal monitoring and control [5]. Despite this success, technical issues like the formation of interfacial layers such as $LiNb_3O_8$ or the diffusion of Li atoms into the grown GaN tend to degrade the electrical and optical properties of the devices. Different growth techniques like pulsed laser deposition or low temperature growth have been suggested to overcome these problems [7–9]. A theoretical investigation of the microscopic LN/GaN interface and the simulation of the GaN growth on LN, fundamental to improve the growth process, are still missing. In this work we simulate the adsorption of a Ga and N monolayers on the LN (0 0 0 1) surface, which represents the first step of the GaN growth on LN, by means of the density functional theory (DFT). The DFT has been proven to be a powerful tool for the investigation of the growth mechanisms of different semiconductors and has been successfully applied to model the growth of polar materials on polar surfaces [10,11]. After briefly illustrating the calculation method and the computational details (Section 2), we discuss the microscopic structure of the LN (0 0 0 1) surface. Bulk LN shows a strong spontaneous electric polarization along the [0 0 0 1] direction (or *z*-axis), which gives rise to two charged and morphologically different surfaces, the positive and the negative LN (0 0 0 1) surfaces. These have been recently the topic of different theoretical and experimental investigations [12–17]. In this work we model the GaN growth on the positive LN (0 0 0 1) surface. The potential energy surfaces (PES) for the adsorption of a single Ga and N atom on the positive LN (0 0 0 1) are calculated both for the ideal as well as for the relaxed surface, in order to find out the adsorption site of the two atomic species. In a second step the adsorption of GaN monolayer

* Corresponding author. Tel.: +49 5251 60 2324; fax: +49 5251 60 3435.
E-mail address: sanna@phys.upb.de (S. Sanna).

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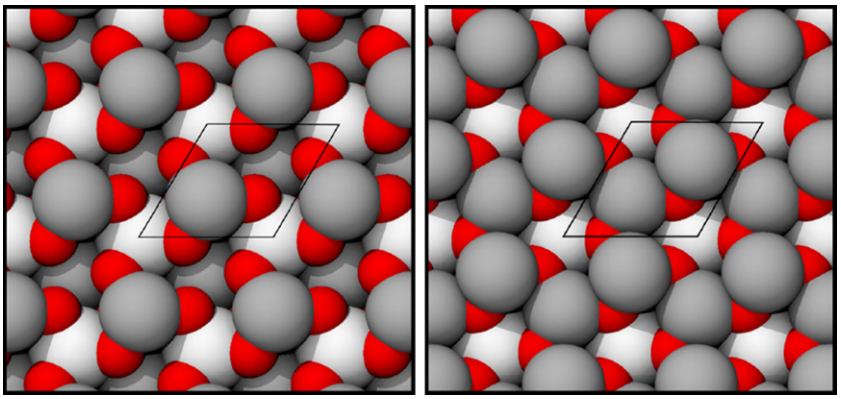

Fig. 1. Atomic structure of the ideal Li-terminated (left hand side) and of the stable relaxed (right hand side) LN (0 0 0 1) surface (top view). Li atoms are represented in gray, Nb in white and oxygen in red. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

is simulated and the properties of the grown material like lattice and polarization orientation are discussed (Section 3). Finally the main results of this investigation are summarized in Section 4.

2. Methods

The density functional theory within the generalised gradient approximation (GGA) as implemented in the VASP simulation package [18] has been used to simulate the bulk phases of LN and GaN, the LN slab modeling the LN(0 0 0 1) surface and the LN/GaN interface. This approach was recently shown to yield reliable structures and energies both for bulk LN (in its paraelectric and ferroelectric phase [19]) and LN surfaces [17].

2.1. Computational

Ferroelectric LN can be considered a stapling of Nb-O_3-Li trilayers along the [0 0 0 1] axis. The slabs for the simulation of the ferroelectric LN (0 0 0 1) surface and the adsorption of Ga and N single atoms are hexagonal supercells consisting of 12 Nb-O_3-Li trilayers (60 atoms) plus a surface termination (for the reconstructed surfaces) and a vacuum layer of ≈15 Å. A bigger cell containing 66 LN substrate atoms (12 trilayer and reconstructed surface) and 6 Ga and N atoms has been used to simulate adsorption of a GaN monolayer. We used the PW91 formulation of the exchange-correlation functional [20] and projector augmented wave (PAW) potentials [21], whereby the Ga 3*d* electrons were included in a pseudo atomic core. The dipole correction described in [22,23] has been used to correct the artificial forces created by the slab images. A Γ centered $2 \times 2 \times 1k$-point mesh was used to carry out the integration in the Brillouin zone. The cutoff for the plane wave basis was 400 eV.

2.2. Modeling the GaN growth

It has been recently shown that both the positive and negative LN (0 0 0 1) surfaces are characterized by a 1×1 reconstruction involving atomic rearrangement and a stoichiometry change relatively to the bulk [14,16,17]. For this reason, we do not consider other slabs than the 1×1 surface unit cell. Because the stoichiometry of the GaN/LN interface is not know yet, we investigate the growth of GaN on both relaxed and ideal LN surfaces (see Fig. 1).

In our model we neglect the effect of the thermal expansion of LN and GaN. Even if it is, in principle, a rather crude approximation (an usual growth temperature is around 600 ° C [9,24]), we think that it will not affect qualitatively our main results. Another issue which is not discussed here regards the capping of the LN sample before GaN growth. Indeed, a buffer layer of AlN or AlGaN has been used in some case to improve the quality of the grown GaN material on ferroelectric substrates [5,8]. We do not simulate the effect of the AlN buffer layer on the GaN growth in this work. This issue will be the object of a future investigation.

3. Results

Fig. 1 shows the ideal Li-terminated and the stable relaxed positive LN (0 0 0 1). Assuming the LN crystal to be a succession of Nb-O_3-Li trilayers piled along the [0 0 0 1] axis, the most stable termination of the positive surface is -Nb-O3-Li_2, whereby one of the topmost Li atoms relaxes in the lower lying oxygen plane. The particular stoichiometry and morphology of the surface have been explained recently [16,17]. In both surfaces represented in Fig. 1 the LN (0 0 0 1) plane has hexagonal symmetry, which seems to be well suited as basis for the coaxial growth of GaN. In particular the oxygen sublattice shows in both cases an hexagonal pattern with a calculate average interatomic distance of 3.04 Å. The interatomic distance of the cations or anions in GaN has been calculated to be 3.25 Å, which yields to a mismatch of 6.9% between the atoms of GaN (0 0 0 1) and the oxygen atoms in LN (0 0 0 1). This is in very good agreement with the nominal mismatch of 6.8% reported in the literature. To determine the stable sites for the adsorption of Ga and N adatoms on LN (0 0 0 1) the potential energy surfaces have been calculated for the two atomic species. Thereby, we sample the unit cell with a dense raster of 48 equally spaced different sites, calculating for each site the adsorption energy. In the PES calculation only the adsorbed Ga or N ions are allowed to relax, perpendicularly to the (0 0 0 1) plane. The threshold for the Hellmann-Feynman forces has been set to 0.02 eV $Å^{-1}$.

Fig. 2 shows the calculated potential energy surface for atomic N and Ga adsorbed on the relaxed (0 0 0 1) surface and Fig. 3 on the ideal (0 0 0 1) surface of ferroelectric LN. The blue regions represent stable sites for the adsorption, while red regions represent sites which are not favorable for the atomic adsorption. The four calculated PES for relaxed and ideal surfaces are qualitatively different: The PES for the N adsorption on the reconstructed LN (0 0 0 1) surface (Fig. 2(a)) shows three almost equivalent adsorption sites centered on the topmost oxygen layer. While nitrogen adsorbs on top of the oxygen atoms, gallium adsorbs on the cationic sublattice (Fig. 2(b)). This difference can be explained as an attempt of the adatom to continue the LN crystal structure with the Ga atoms on the cationic site and N atoms at anionic sites. Nitrogen adsorbs 1.36 Å above the underlying oxygen and gallium 2.89 Å above the underlying Nb, i.e. 1.16 Å above the outmost Li-layer. Concerning the ideal structure (Fig. 3(a) and (b)), both N and Ga tend to avoid the topmost Li-layer, however no pronounced preference of the N atoms for the oxygen sublattice can be observed. In this way the pattern for the quasi lattice matched growth of GaN on LN (0 0 0 1) is

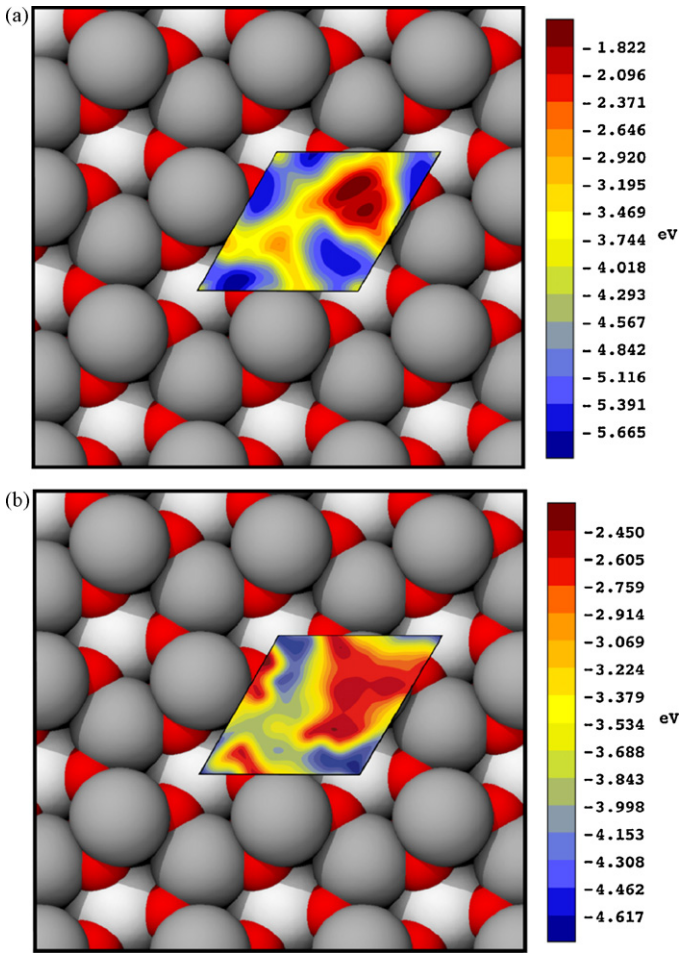

Fig. 2. Potential energy surface for the adsorption of a single N atom (a) and Ga atom (b) on the positive reconstructed $LiNbO_3$ (0 0 0 1) surface. Li atoms are represented in gray, Nb in white and oxygen in red. The 1×1 hexagonal unit cell of $LiNbO_3$ is highlighted. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

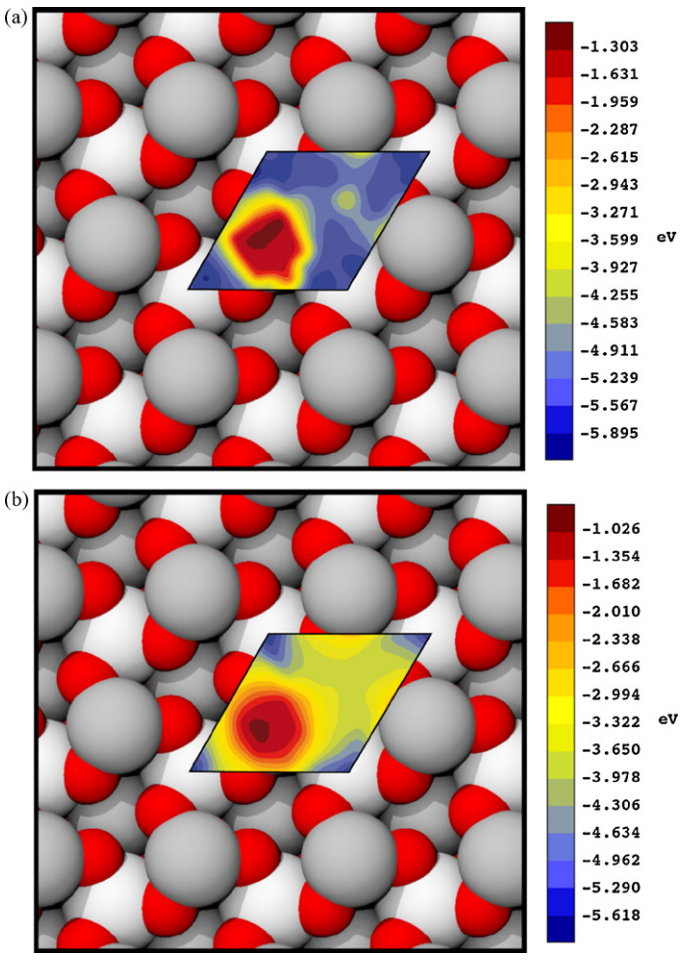

Fig. 3. Potential energy surface for the adsorption of a single N atom (a) and Ga atom (b) on the positive, ideal, Li-terminated, $LiNbO_3$ (0 0 0 1) surface. Li atoms are represented in gray, Nb in white and oxygen in red. The 1×1 hexagonal unit cell of $LiNbO_3$ is highlighted. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

missing. Surface relaxation (or reconstruction), adsorption of atoms molecules as well as electronic passivation are common mechanisms which occur on polar surfaces to yield to a more stable configuration. For this reason it is not surprising that the ideal and the relaxed (*stabilized*) surface behave differently as substrate for the adsorption of the same ions.

The calculated PESs also give informations about the migration paths and migration barrier energies for the adatoms on the surface, however they are not discussed in detail in this work.

Let us concentrate at first on the reconstructed surface. The adsorption energy of the two ions, which we define as the energy necessary to pick one adatom from the surface and bring it to infinity, is quite different: a single N atom on the 1×1 surface cell is more strongly bound to the substrate than a single adsorbed Ga by an energy of around 1.5 eV. As a result a N monolayer (three atoms on the 1×1 surface unit cell) is more strongly bound than a Ga monolayer on the LN (0 0 0 1) surface. For this reason we start with a nitrogen monolayer the simulation of the adsorption of the first GaN monolayer on LN. Following the approach of Fujiwara et al. [10] we simulated the adsorption of a GaN monolayer comparing the total energies of different structural models of the LN/GaN interface. As before, we employed a 1×1 periodicity and calculate the total energies fixing the layer laterally and allowing the height to relax. Starting from the N layer discussed before and shown in Fig. 4, we pick a single N atom, which we use as reference (see arrow in

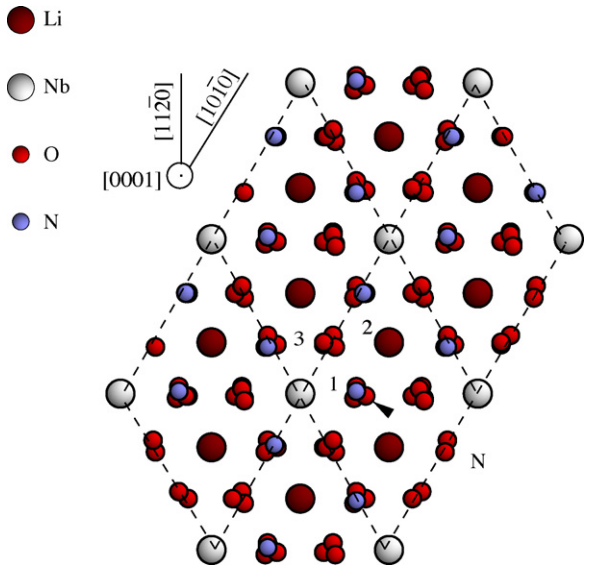

Fig. 4. Atomic structure of the positive LN (0 0 0 1) surface with adsorbed N (top view). The LN surface unit cell is highlighted and the main LN crystallographic directions are indicated.

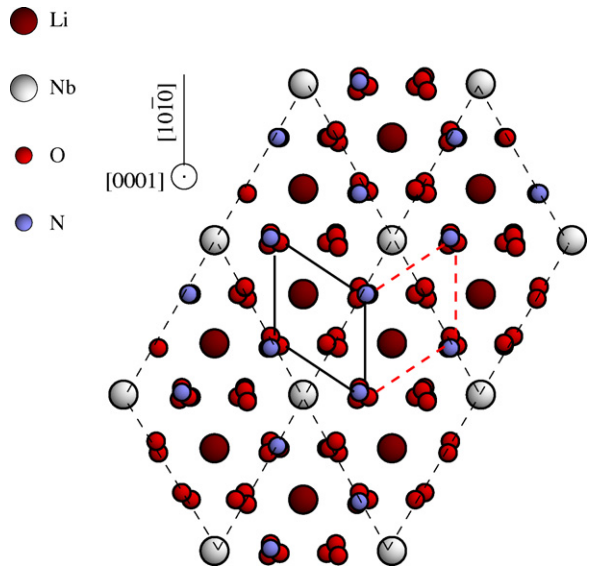

Fig. 5. Atomic structure of the positive LN (0 0 0 1) surface with adsorbed N (top view). The surface unit cell of the adsorbed GaN layer is highlighted with the solid black line. The dashed line represents another possible but energetically disadvantaged growth orientation. Note that the two GaN unit cells are not equivalent. The crystallographic axes refer to the GaN system and can be compared with the LN crystallographic axes of Fig. 4.

Fig. 4). There are three prominent different positions for the adsorption of a Ga atom and the building of a GaN monolayer: on top of the N atom itself (see point 1 in Fig. 4) on top of the cations (Li or Nb atom, shown as position 2 in Fig. 4) or on top of an O atom (position 3 in Fig. 4). In the first case, the GaN monolayer would be the first step of a GaN growth along the GaN [0 0 0 $\bar{1}$] direction, while in the last two cases GaN would grow along the [0 0 0 1] direction. In the case of a growth along the [0 0 0 1] direction, the *c*-axes of GaN and LN would be parallel, otherwise antiparallel. The adsorption of a Ga atom on position 2 in Fig. 4 is energetically disadvantaged, as the Ga adsorption on the topmost Li is not a stable configuration (see PES in Fig. 2). Furthermore, due to the different height of the adsorbed N and Ga the resulting Ga-N bond is stretched with respect to the bulk value of 1.98 Å. Of the remaining possibility, the Ga adsorption on another oxygen site (point 3 in Fig. 4) is favored by 1.43 eV per GaN unit formula with respect to the adsorption on N itself (point 1 in Fig. 4). This means that the *c*-axis of the emerging GaN would be parallel to the substrate *c*-axis.

In Fig. 5 we show the unit cell of the adsorbed GaN monolayer (solid black line). The crystallographic axes in the picture refer to the adsorbed layer and can be compared with the crystallographic axes of LN reported in Fig. 4. It is evident that the LN [1 1 $\bar{2}$ 0] axis is parallel to the GaN [1 0 $\bar{1}$ 0] axis, i.e. the two cells are rotated by 30°.

3.1. Discussion

Even if the LN is usually described as rhombohedral crystal, it also possesses hexagonal symmetry and can be represented by an hexagonal unit cell [25]. The LN *c*-plane is similar to the sapphire *c*-plane and can be used as basis for the growth of wurtzite GaN.

The main difference with α-Al_2O_3 is, apart from the different lattice constant, the pronounced spiral staircase nature of the oxygen octahedra along the [0 0 0 1] axis, which results in a larger dispersion of the oxygen positions around the central locations than in sapphire. On turn, this results in a small rotation of the oxygen sublattice with respect to the cation sublattice. For this reason the (0 0 0 1) planes of LN and GaN are rotated by an angle which is slightly larger than exactly 30°. This in-plane lattice relation minimizes the lattice mismatch between GaN and LN and is, although unusual, energetically favored. The calculated in-plane lattice mismatch between LN and GaN (6.9%) is in good agreement of the nominal value of 6.8%. The out of plane lattice relation instead cannot be estimated by the growth of a single GaN monolayer.

4. Summary

In this work we have investigated the adsorption of a GaN monolayer on the LN (0 0 0 1) surface by means of DFT total energy calculations. Firstly the stable sites for the adsorption of single N and Ga atoms on the relaxed and on the ideal (not relaxed) LN (0 0 0 1) surface have been individuated. Nitrogen adsorbs on the reconstructed surface on the oxygen site, while Ga prefers the cationic site. In this way a single N layer (which is found to be more strongly bound to the substrate than a Ga layer) has the ideal pattern for a quasi lattice matched growth of GaN on LN. The successive adsorption of the Ga atoms occurs in such a way that the GaN and $LiNbO_3$ (0 0 0 1) planes are parallel, but rotated by 30°. The in-plane epitaxial relationship between the two materials is therefore $[1\,0\,\bar{1}\,0]_{GaN} \parallel [1\,1\,\bar{2}\,0]_{LiNbO3}$. This in-plane lattice relation minimizes the lattice mismatch between GaN and $LiNbO_3$.

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