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GaN growth on $LiNbO_3$ (0001) – a first-principles simulation

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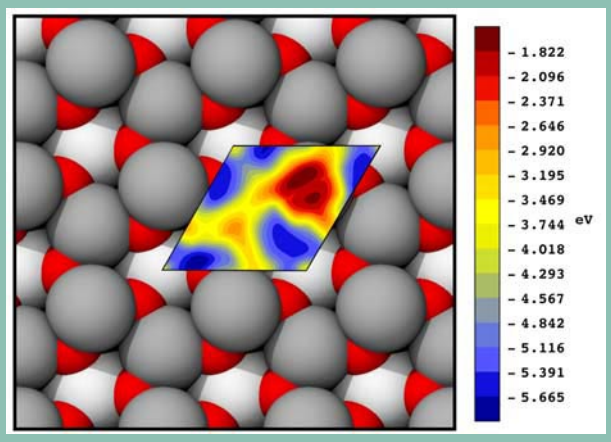
The growth of GaN on the $LiNbO_3$ (0001) surface is simulated by means of first-principles total-energy calculations. Firstly the adsorption of single N and Ga monolayers is investigated and then the layer-by-layer growth of GaN on the polar substrate within different orientations is modeled. While adsorbing a N layer does not heavily affect the substrate morphology, the adsorption of a Ga layer causes a rearrangement of the atomic structure. Furthermore the N layer is more strongly bound to the substrate than the Ga layer. On the basis of our results, we propose a microscopic model for the GaN/$LiNbO_3$ interface. The GaN and $LiNbO_3$ (0001) planes are parallel, but rotated by 30° each other, with in-plane epitaxial relationship $[10\bar{1}0]_{GaN} \parallel [11\bar{2}0]_{LiNbO_3}$. In this way the (0001) calculated in-plane lattice mismatch between GaN and $LiNbO_3$ is minimal and equal to 6.79% of the GaN lattice constant.



(Color online) Potential energy surface for the adsorption of a single N atom on the positive $LiNbO_3$ (0001) surface. Li atoms are represented in gray, Nb in white and oxygen in red.

1 Introduction The lack of a native substrate for the III-nitrides represents a major drawback for many applications. Epitaxially grown GaN is affected by a high density of lattice defects, due to the considerable lattice mismatch (around 16%) between GaN and α-Al_2O_3, the most widely used substrate [1]. This might not be relevant for the realization of devices like light emitting diodes [2], but certainly represents a major issue for the realization of devices which require a precise band engineering (e.g. Schottky-junctions). To overcome this problem $LiNbO_3$ (LN) has been recently proposed as a new substrate. LN is characterized by a relatively small lattice mismatch with respect to GaN and an outstanding cost-performance ratio [3–5]. The (0001) plane of LN has, just like α-Al_2O_3, hexagonal symmetry and provides a nominal lattice mismatch of only 6.8% with the GaN (0001) plane, which results in a better GaN crystal quality. The key advantage of this substrate is, however, the possibility to use the LN polarization to control the GaN growth, allowing new polarization engineered structures. For example, GaN/LN heterostructures were grown in order to realize acoustic filters [4]. Despite this success, there are still technical issues which tend to degrade the electrical and optical properties of the devices (formation of $LiNb_3O_8$ interfacial layer, diffusion of Li atoms into GaN). Furthermore both a theoretical investigation of the LN/GaN interface and the simulation of the GaN growth on LN are still missing. In an attempt to improve the understanding of the growth process, which is indispensable to optimize and fully implement GaN/LN based devices, we simulate the layer-by-layer growth of GaN on

LN(0001) by means of the density functional theory. Bulk LN shows a strong spontaneous electric polarization along the [0001] direction (or z-axis), which gives rise to two charged and morphologically different surfaces, the positive and the negative LN (0001) surfaces. In this work we simulate the GaN growth on the positive surface. Firstly we model the adsorption of single Ga and N monolayers on the surface and their effect on the substrate, then the layer-by-layer growth of GaN is simulated and the properties of the grown material like lattice and polarization orientation are discussed.

2 Methods Density functional theory (DFT) total energies of LN and LN/GaN slabs as well as bulk Ga, LN, GaN and N_2 dimers have been obtained using projector augmented wave (PAW) potentials [13] and the PW91 formulation of the generalized gradient approximation [14] as implemented in the VASP simulation package [15]. Thereby the Ga $3d$ electrons were included in a pseudo atomic core. This approach was recently shown to yield reliable structures and energies both for bulk LN [16] and LN surfaces [12]. The slabs for the simulation of the layer-by-layer growth of GaN on LN (0001) are hexagonal supercells consisting of 66 substrate atoms plus up to 24 Ga and N atoms and a vacuum layer of at least 15 Å. All the GaN atoms and 12 LN layers were allowed to relax (force threshold 0.02 eV/Å). The dipole correction described in [17,18] has been used to correct the artificial forces created by the slab images. A Γ centered $2\times2\times1$ k-point mesh was used to carry out the integration in the Brillouin zone. The cutoff for the plane wave basis was 400 eV.

Different approximations have been adopted to model the LN/GaN interface formation. First of all, thermal expansion effects (GaN is usually grown on LN at temperatures around 870 K [7]) are not taken into account. Possibly more important, we assume an atomically flat interface where no stoichiometric changes with respect to the clean substrate surface occur. While the stability of the substrate at high temperatures (the transition phase to the paraelectric structure takes place at 1480 K) as well as the very stable configuration of the LN (0001) surface render stoichiometric changes at first sight unlikely, future studies will need to address the issue in more detail. Also the effect of a buffer layer (e.g. AlN), which has been used in some experiment to improve the quality of the grown material [4,6] is not considered in this work.

3 Results The LN (0001) surface has been recently investigated both theoretically and experimentally [8–12]. RHEED and LEED measurements have shown that the surface has 1×1 periodicity [9], while theoretical investigations have shown that the positive termination is -Nb-O_3-Li_2 [11,12]. In particular, one of the Li atoms in the topmost layer relaxes down into the lower lying oxygen plane, while the other remains above it, as represented in the abstract picture. The oxygen sublattice on the surface shows an hexagonal pattern with an average interatomic distance which we calculate to be 3.040 Å. The interatomic distance of the cations or anions in GaN has been calculated to be 3.247 Å, which yields to a mismatch of 6.798% between the atoms in the GaN (0001) plane and the oxygen atoms in LN (0001). Indeed, potential energy surfaces (PES) calculations for the adsorption of single N and Ga atoms on the positive LN (0001) have shown that N atoms adsorb on top of the oxygen atoms (see abstract picture), while Ga prefers the cationic site [19]. Though, in the quasi lattice matched growth of GaN on LN, the unit cell of LN is thrice as big as the GaN unit cell, i.e. the adsorption of a whole Ga or N monolayer is represented by three adatoms on the LN unit cell. We have investigated this configuration starting with the adatoms in different positions and fully relaxing both the three adatoms and the surface. Our calculations show that in this case the stable adsorption site for Ga atoms becomes on top of the oxygen lattice, while N atoms tend to leave the oxygen sublattice to adsorb closer to the lower lying Li atom. This means the N atoms in the adsorbed N layer do not mirror the oxygen sublattice, however they become again equally spaced after the adsorption of a further Ga monolayer. The adsorption of a single N monolayer causes an almost negligible relaxation of the LN (0001) surface, while the adsorption of a single Ga monolayer causes the topmost Li layer to relax down into the lower lying oxygen plane, as shown in Fig. 1. We define the binding energy of an adatom as the energy necessary to separate it from its reference phase and adsorb it on the considered surface. The binding energy is therefore not universally defined, as it refers to the atomic phase used as atomic source during the growth. The binding energy of an N atom in a single adsorbed N monolayer, calculated with respect to the gas phase (N_2), is 1.438 eV, while the

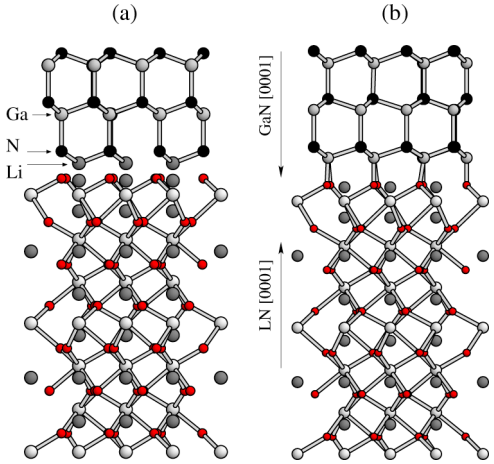


Figure 1 (Color online) The LN/GaN interface in case of GaN growth starting with a N layer (a) or a Ga layer (b). In both cases the [0001] axes of GaN and LN have the opposite orientation.

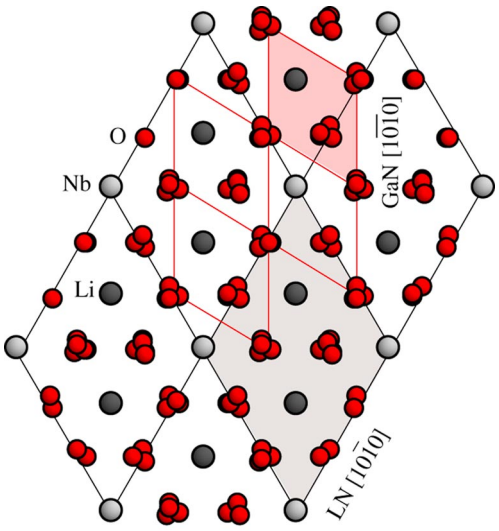


Figure 2 (Color online) The relative orientation of the LN (large one) and GaN (small one) unit cells in the (0001) plane.

adsorption energy of a Ga atom in a single adsorbed Ga monolayer, calculated with respect to the stable bulk phase (α-Ga), is 0.811 eV. This means that a single N monolayer is more strongly bound to the substrate than a single Ga layer.

After the adsorption of a first monolayer, there are two stable positions for the adsorption of a monolayer of the other atomic type, either with the atoms on top or between the atoms of the first monolayer, so that they result on top of another oxygen site. Depending on the layer succession, these two possibilities will result into the growth along the [0001] and along the [000$\bar{1}$] direction. In both cases the direction of the [0001] crystallographic axes of LN and GaN is parallel, furthermore the LN [11$\bar{2}$0] axis is parallel to the GaN [10$\bar{1}$0] axis, i.e. the two cells are rotated by 30°, as shown in Fig. 2. This crystallographic relationship is, even if unusual, the one which minimizes the lattice mismatch between the two materials. Summarizing, the growth of GaN can begin either with a Ga or with a N layer and in both cases can be continued so that the c-axis of GaN and LN are parallel or antiparallel (see Fig. 1). We have modeled the layer-by-layer growth for each of the four possibilities, confirming that GaN always grows along the [0001] or along the [000$\bar{1}$] direction.Work is in progress to find out under which conditions GaN grows with the c-axis parallel or antiparallel to the LN c-axis and if the polarization vectors of the two materials have the same orientation or are directed against each other.

4 Summary In this work we have presented the first theoretical investigation of the GaN growth on LN (0001). The adsorption of single Ga and N atoms and monolayers on the LN (0001) have been simulated and the layer-by-layer GaN growth has been modeled. A single Ga monolayer is found to introduce a rearrangement of the atomic positions and to be less bound to the substrate than a single N monolayer, which does not cause any major atomic relaxation. LN and GaN [0001] axes have the same direction (coaxial growth), however their orientation (parallel or antiparallel) has not been determined yet. The (0001) planes of substrate and grown layer are rotated by 30° each other, with in-plane epitaxial relationship $[10\bar{1}0]_{\mathrm{GaN}} \parallel [11\bar{2}0]_{\mathrm{LiNbO_3}}$. This relatioship has been recently observed in RHEED measurements [6] and is the one which minimizes the lattice mismatch between GaN and $LiNbO_3$.

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