

Investigation into the Adsorption of Atomic Nitrogen on an Al_2O_3 (0001) Surface

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Abstract—Computer simulation of sapphire nitridation used to obtain nitride-based heterostructures (GaN) on an Al_2O_3 substrate has been performed. The adhesion of atomic nitrogen to the sapphire (0001) surface is investigated ab initio. The possibility of replacing surface-layer oxygen atoms with nitrogen atoms has been examined. The calculated results indicate that adsorbed nitrogen atoms occupy the most stable positions above surface oxygen atoms at different nitrogen concentrations. The changes in the total system energy after replacement of surface oxygen atoms with nitrogen atoms have been calculated. It turns out that oxygen replacement is energetically unfavorable for a single nitrogen adatom. However, this process becomes energetically favorable if the concentration of nitrogen atoms increases. This outcome, obtained for the first time, enables better understanding of the atomic-scale mechanism of sapphire nitridation.

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INTRODUCTION

In the last decade, researchers has expressed increased interest in wide band gap materials (AlGaIn, GaN, InN, diamond, etc.), which are considered promising semiconductors in the manufacturing of new electronic and optoelectronic devices. Among them, GaN possesses unique properties and is a universally recognized semiconducting material of the next generation. As materials used to manufacture microwave transistors, multilayer structures based on wide band gap semiconductors exhibit a number of fundamental advantages. In particular, their application provides ample possibilities for varying the energy-band structure of devices and producing a 2D electronic gas with a high concentration of charge carriers [1].

To grow heterostructures with nanosized layer thicknesses, knowledge of the interfaces of the microstructures and understanding of the mechanism of the initial growth stages are of principal importance. Sapphire is a promising material for application as substrates for nitride-based heterostructures. Since Al_2O_3 and GaN have substantial lattice-period mismatch (~16%) and the difference between their thermal-expansion coefficients is very large (~34%), GaN epitaxial growth on sapphire is accompanied by the appearance of a great number of dislocations. Hence, low-quality heterostructures are formed. With the use of an AlN buffer layer, the mismatch of the AlN and GaN lattice periods is insignificant (~3%), ensuring significant improvement in the crystalline structure and properties of GaN layers on sapphire [2]. The most widespread approach to producing thin monoc-

crystalline AlN films on sapphire is substrate nitridation via molecular beam epitaxy [3] and gas-phase epitaxy [4]. In these experiments, ammonia serves as a highly reactive nitrogen source. As a result of nitridation caused by ammonia adsorption on the sapphire surface, nitrogen atoms penetrate into the substrate, modifying its structure so that a thin aluminum nitride layer is formed. Despite a determinative role in the formation of a buffer layer, this process is little studied theoretically and experimentally. The authors of [3, 5] who performed the nitriding of sapphire (0001) substrates by means of molecular beam epitaxy and hydride vapor-phase epitaxy have proposed a nitridation model based on their experimental data. This model involves the following interrelated processes:

- (i) Ammonia adsorption on the sapphire surface.
- (ii) Ammonia dissociation accompanied by the desorption of molecular hydrogen or water molecules and atomic nitrogen adsorption on the surface.
- (iii) Atomic nitrogen diffusion through an AlN layer to the reaction front in the sapphire substrate.
- (iv) Replacement of oxygen atoms with nitrogen atoms in the sapphire structure.
- (v) Atomic oxygen diffusion through the AlN layer to the surface and transformation of the Al_2O_3 structure into that of AlN.

The nitridation process can only be understood by establishing the atomic-scale mechanisms of all stages listed above. In this work, the adsorption process of nitrogen atoms on an Al_2O_3 (0001) surface was investigated theoretically in the scope of density functional theory. Moreover, the energies for the replacement of oxygen atoms with nitrogen atoms within the Al_2O_3

(0001) surface layer were calculated to study the possibilities of this replacement.

THEORY

The investigation was performed in the context of electron density functional theory using plane waves and PAW potentials as a basis [6]. Calculations were carried out by means of the Vienna ab initio simulation package (VASP) [7]. The structure of the sapphire (0001) surface was simulated in an approximation of periodic crystal plates with the help of periodic supercells. For this purpose, (1×1) 30-atom supercells comprising six layers of oxygen atoms and 12 layers of aluminum atoms and (2×2) 60-atom supercells including three layers of oxygen atoms and six layers of aluminum atoms were employed. To reduce the size of the (2×2) calculation cells, the coordinates of the atoms constituting the four bottom atomic layers were fixed in position corresponding to an Al_2O_3 single crystal. The vacuum-layer thickness was selected so that the two surfaces formed by the plate were noninteracting due to periodic boundary conditions.

An exchange-correlation interaction was described via the local density approximation. In the calculations, magnetic interaction was taken into account. The relaxation of forces acting on the ions was achieved by means of the conjugate-gradient method. The dynamic relaxation of atoms was performed until the variation in the system energy became less than 0.001 eV. In this case, the residual forces acting on ions were less than 0.01 eV/Å. After performing test calculations on the sapphire single crystal, the cutoff energy of the basis of the plane waves was chosen to be 600 eV. The electron structure was calculated by integration over the Brillouin zone with the help of a k -point mesh constructed according to the Monkhorst–Pack method [8]. For (1×1) and (2×2) cells, the sizes of the k -point mesh were $8 \times 8 \times 1$ and $4 \times 4 \times 1$, respectively. The presented values of the aforementioned parameters of the calculation scheme were sufficient to ensure reliable results. All calculations were performed using supercomputers at the Interdepartmental Supercomputing Center, Russian Academy of Sciences.

RESULTS AND DISCUSSION

From geometric considerations, the sapphire (0001) surface can be bounded by three variants: an atomic layer of oxygen, an atomic layer of aluminum, or two atomic layers of aluminum (Fig. 1). According to experimental data [9, 10] and ab initio calculations [11, 12], the second variant, i.e., an atomic layer of aluminum, is stable. Hence, in this study, a sapphire (0001) surface bounded by an aluminum layer was considered. It should be noted that the calculated relaxation of the top aluminum layer (86% of the equilibrium distance between the oxygen and aluminum

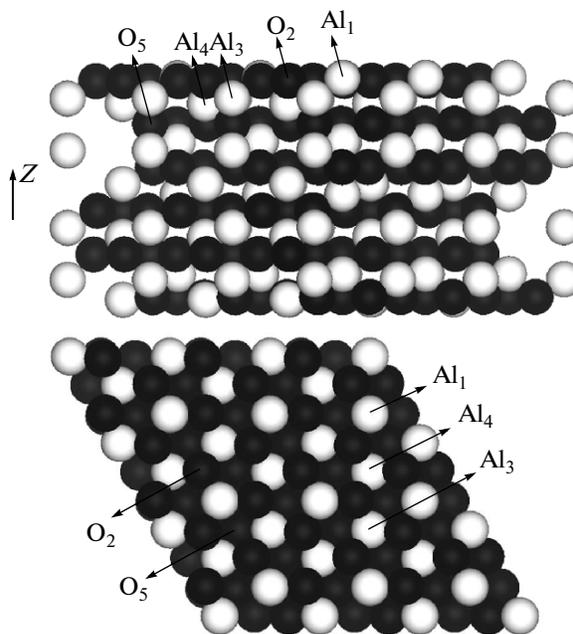


Fig. 1. Diagrammatic representation of the sapphire (0001) surface and five highly symmetric positions therein. Aluminum and oxygen atoms are colored white and black, respectively.

planes in the sapphire single crystal) is close to the values obtained with the help of ab initio calculations in the scope of the density functional method: 82% [11] and 90% [13].

Thus, the chosen calculation scheme enables correct description of the sapphire surface's structure. As a result of such high relaxation, an aluminum atom (Fig. 1, Al_1) descends almost to the level of the lower-lying atomic layer of oxygen (Fig. 1, O_2): the distance between the aluminum and oxygen layers is only 0.12 Å.

An adsorbed nitrogen atom can occupy one of five highly symmetric positions on the sapphire (0001) surface, which are designated by the symbols Al_1 , O_2 , Al_3 , Al_4 , and O_5 in Fig. 1. With allowance for the aforesaid, Al_1 and O_2 are positions above surface atoms, and Al_3 , Al_4 , and O_5 are interstitial sites arranged above aluminum and oxygen atoms, respectively. To describe the adsorption of a single nitrogen atom on the sapphire surface, (2×2) cells were selected in the XY plane. Such selection of cells leads to the fact that the distance between adjacent nitrogen atoms is about 9.5 Å, making it possible to prevent interactions between adsorbed atoms and their own reflections caused by the periodic boundary conditions. The calculated adsorption energies of a nitrogen atom corresponding to the five positions listed above are presented in the table. According to these values, O_2 is the most stable position when nitrogen atoms are adsorbed on the sapphire (0001) surface. In this case, the typical adsorption energy is -2.00 eV. The interstitial site above an oxygen atom is less favorable (the adsorption energy is

Calculated adsorption energies of a single N atom

Position	E , eV
Al ₁	-0.90
O ₂	-2.00
Al ₃	-0.22
Al ₄	-0.24
O ₅	-1.57

-1.57 eV). The interstitial sites above the subsurface aluminum atoms (with almost equal adsorption energies of -0.22 and -0.24 eV) are least energetically favorable. The proximity of these energies is explained by the fact that, along the Z axis corresponding to the [0001] axis of the Al₂O₃ crystal, the difference between the heights of the two atoms is only 0.27 Å.

In calculations of the adsorption energy, a nitrogen atom is surrounded by 12 subsurface oxygen atoms. However, the adsorbed-nitrogen concentration can be much higher under experimental conditions because the sapphire substrate is bombarded by ammonia molecules. In connection with this, nitrogen adsorption calculations were performed at higher concentrations corresponding to one-third of a monolayer and an entire monolayer. According to [14], the monolayer on the sapphire (0001) surface is characterized by an adatom concentration at which each adsorbate atom corresponds to a subsurface oxygen atom. Accordingly, in the case of one-third of a monolayer, a nitrogen adatom coexists with three subsurface oxygen atoms.

For the adsorption of nitrogen with a concentration corresponding to one-third of a monolayer, five highly symmetric positions of adsorption (similar to those of a single adatom) were considered. In this case, the O₂ position, the typical adsorption energy of which

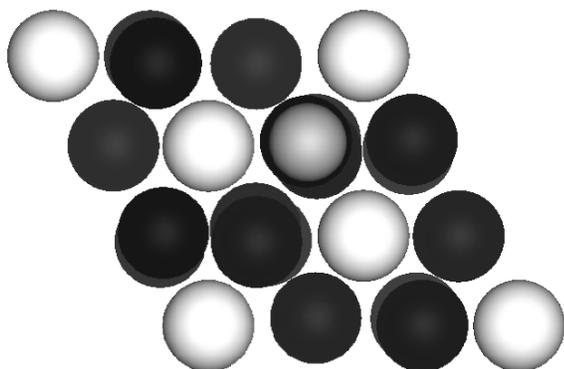


Fig. 2. Diagrammatic representation of the (1 × 1) cell on the sapphire (0001) surface. Adsorbed nitrogen with a concentration corresponding to one-third of a monolayer is located at the O₂ position. Aluminum, oxygen, and nitrogen atoms are colored white, black, and grey, respectively.

is -2.08 eV per nitrogen atom, remains most energetically favorable (Fig. 2).

For the adsorption of nitrogen with a concentration corresponding to an entire monolayer, three situations were considered: three nitrogen adatoms are located above three O₂ positions (Fig. 3a), three O₅ positions (Fig. 3b), or the Al₁, Al₃, and Al₄ positions (Fig. 3c). In this case, adsorption at O₂ positions also remains most energetically favorable, and the adhesion energy is -2.12 eV per nitrogen atom. Moreover, it should be emphasized that, according to the performed calculations, nitrogen atoms can combine together due to collective interaction and form a N₃ cluster in the shape of an equilateral triangle with the center located above the Al₁ position (Fig. 4). In this case, the triangle side (N-N bond) is 1.36 Å. Note that the height of the trimer is about 3 Å above the surface, and its adsorption energy is -0.02 eV. Thus, calculations indicate that small nitrogen clusters can be physically adsorbed on the sapphire surface, thereby hindering the nitridation process.

Since the sapphire-surface-nitridation models proposed in the published works [3, 5] rely on the replacement of substrate oxygen atoms with nitrogen ones, the possible replacement of a subsurface-layer oxygen atom (Fig. 1, O₂ layer) with nitrogen atoms was investigated. In this case, the oxygen atom released from the subsurface layer occupied different possible positions of adsorption on the surface (Fig. 1). For a single nitrogen atom, calculations were carried out in the (2 × 2) cell. It follows from the calculated data that the replacement of a surface oxygen atom on the sapphire (0001) surface is energetically unfavorable with the use of a single nitrogen adatom. This is confirmed by an increase in the total system energy. A situation where the replaced oxygen atom was located at the O₂ adsorption position above the oxygen atom of a subsurface layer is illustrated in Fig. 5. Owing to the aforementioned replacement, the increase in the total system energy is 2.55 eV (per nitrogen atom) compared to the system with a nitrogen atom adsorbed at the O₂ position (the most stable position for the adsorption of a single nitrogen atom).

The replacement process was also examined when the adsorbed-nitrogen concentrations corresponded to one-third of a monolayer and an entire monolayer. The calculated data indicate a quantitative change in the system's energy. If the adsorbed-nitrogen concentration corresponds to one-third of a monolayer, the replacement of an oxygen atom with a nitrogen atom and the adsorption of the replaced oxygen atom above the O₅ position reduce the total system energy by 0.36 eV per nitrogen atom.

In the case where the adsorbed-nitrogen concentration corresponds to an entire monolayer, the replacement of a subsurface-layer oxygen atom with a nitrogen atom with subsequent adsorption of the replaced oxygen atom above the O₂ position leads to a decrease in the total system energy by 0.27 eV per

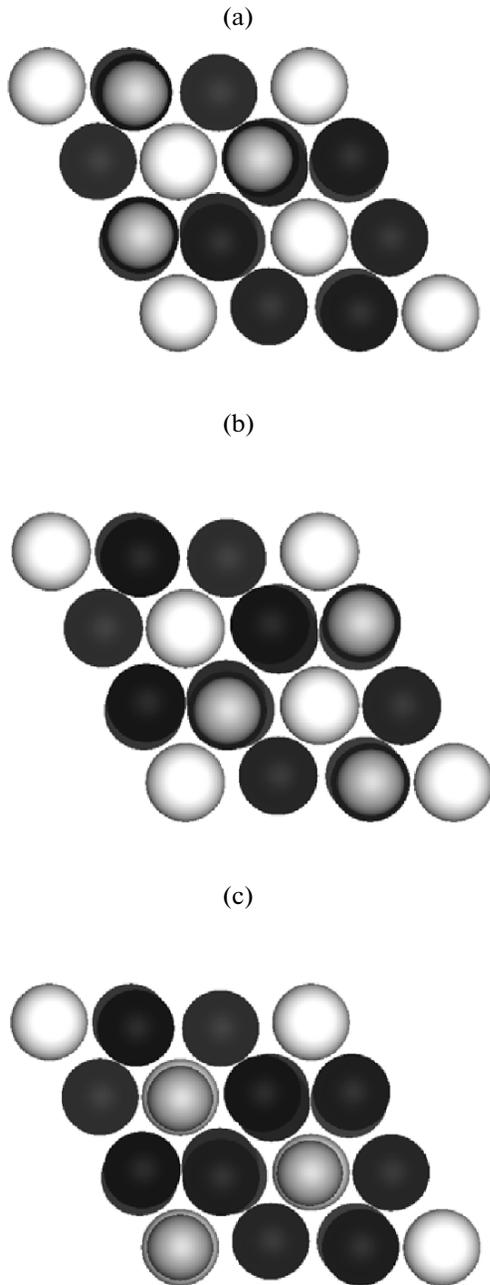


Fig. 3. Diagrammatic representation of the (1×1) cell on the sapphire (0001) surface. Adsorbed nitrogen with a concentration corresponding to an entire monolayer is located at the positions (a) O_2 , (b) O_5 , and (c) Al_1 , Al_3 , and Al_4 . Aluminum, oxygen, and nitrogen atoms are colored white, black, and grey, respectively.

nitrogen atom. The simultaneous replacement of two oxygen atoms with nitrogen ones reduces the total system energy by 0.58 eV.

Thus, if the adsorbed-nitrogen concentration on the sapphire (0001) surface increases due to the collective interaction of nitrogen adatoms, it is energeti-

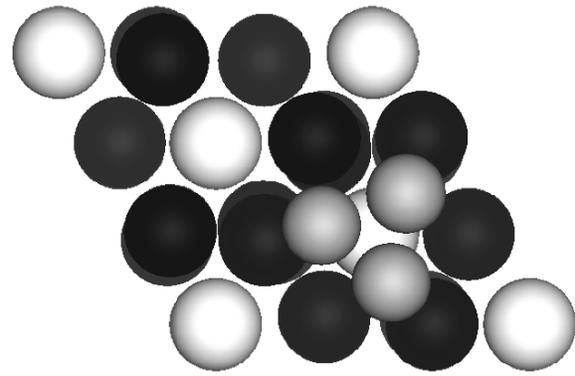


Fig. 4. Diagrammatic representation of the (1×1) cell on the sapphire (0001) surface. The adsorbed nitrogen creates a N_3 trimer. Aluminum, oxygen, and nitrogen atoms are colored white, black, and grey, respectively.

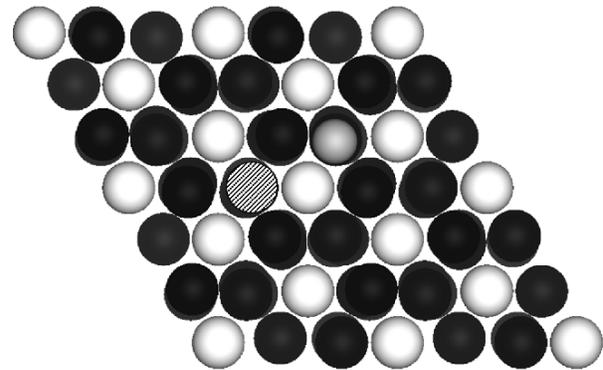


Fig. 5. Diagrammatic representation of the (2×2) cell on the sapphire (0001) surface. An oxygen atom of the subsurface layer is replaced with a nitrogen atom. The replaced oxygen atom is adsorbed on the sapphire surface at the O_1 position. Aluminum, oxygen, and nitrogen atoms are colored white, black, and grey, respectively. The adsorbed oxygen atom is shown by hatching.

cally preferable to replace the oxygen atoms of the subsurface layer of a substrate with nitrogen atoms. It should be noted that this process has an analogy, in particular, when carbon atoms with a sufficiently high concentration are adsorbed on an iron (001) or (111) surface: collective interactions can lead to the immersion of adsorbed atoms in the subsurface layer and the formation of an interstitial solid solution [15]. The obtained results can play a key role in understanding the mechanism behind sapphire-substrate nitridation.

CONCLUSIONS

An ab-initio theoretical investigation, aiding in understanding the mechanism of nitridation of a sapphire (0001) surface at the initial stage of semiconductor heterostructure growth, has been performed. In particular, it has been revealed that the position above

a surface oxygen atom is energetically preferable from the viewpoint of the adsorption of a monoatomic nitrogen layer on the given surface at different concentrations of adsorbed nitrogen. Although the replacement of a surface oxygen atom is energetically unfavorable with the use of a single nitrogen atom, the replacement process is demonstrated to become energetically preferable with increasing nitrogen concentration. The calculated results enable us to infer that the nitridation process requires adsorbed-nitrogen concentrations equal to or greater than one-third of a monolayer.

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