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Research Article

Structural and Electronic Properties of GaN (0001)/α-Al_2O_3 (0001) Interface

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Structural and electronic properties of the interface between α-Al_2O_3 (0001) and GaN (0001) surfaces are investigated through *ab initio* calculations within the density functional theory. Two different structural models have been investigated interface N(Ga)-terminated. The interface N-terminated GaN surface seems to exhibit the lowest formation energy. The studied interface models are metallic, with the levels at energy spatially confined in the interface region. Our calculations show strong hybridization between atoms in the interface region.

1. Introduction

Investigation of physical properties of group III-nitrides such as InN, AlN, and GaN is interesting of basic research and for possible applications. The gallium nitride (GaN) specially, which has a direct energy gap of 3.4 eV [1], has attracted great attention due to its intriguing optoelectronic properties and high thermal and mechanical stability. Energy gap engineering of their ternary alloys allows the tuning of their physical properties for applications such as light emitting diodes (LEDs) and laser diodes covering the spectral wavelength from infrared to ultraviolet [2]. The GaN has the ability to operate in harsh environments and high voltage conditions, where Si based devices experience electrical breakdown, is particularly attractive [3]. For optoelectronic applications at room temperature, the GaN must be of high purity and high crystalline quality with a low defect density. Although GaN is a material of interest for various applications, growing the sample is not a simple task because the growth depends on the used substrates.

Currently, the techniques most commonly used to grow GaN are chemical vapor deposition (CVD) and molecular beam epitaxy (MBE). In the growth by CVD high temperatures ranging from 900 to 1050°C are used, which limits the choice of substrate. In MBE it is possible to grow at lower temperatures such as 700°C; however, the method has high running costs and is limited to small substrates [4, 5]. An alternative is the conventional metal oxide (insulator) semiconductor field effect transistor (MOSFET), with GaN and a high dielectric constant (high-k) material as the semiconductor and oxide (insulator), respectively. Investigations of the high-k/GaN interfaces are very common in literature [6, 7] but still have much to be learned. In particular, investigation of the high-k/GaN interface quality through capacitance/conductance voltage measurements may not necessarily lead to a full understanding of the interface state density across the semiconductor band gap.

Sapphire (Al_2O_3) is an attractive candidate one for the high-k material, with a dielectric constant of ≈8 [8] and a wide band gap of ≈6.6 eV [9], for amorphous aluminum oxide typical of ALD-grown layers, favorable band alignments with GaN [10], and good thermal stability.

Ab initio calculations are the best theoretical methodology to understand the electronic properties and energetic stability when considering the interface between different materials. In this paper, we calculate the structural, electronic, and energetic properties of Al_2O_3/GaN interface using *ab initio* calculations. We find that the energetic behavior of this interface depends on the polarity of the GaN surface.

2. Methodology

The calculations are performed in the framework of the density theory (DFT) [11] with the generalized gradient

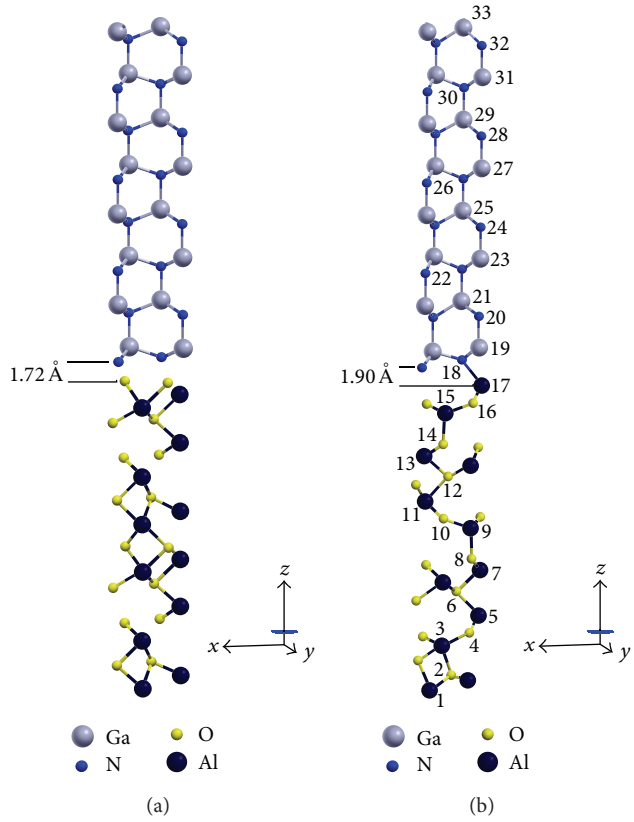

FIGURE 1: (a) Unrelaxed and (b) relaxed structure of the unit cell of GaN/Al_2O_3 N-terminated interface.

approximation (GGA) parameterized by Perdew, Burke, and Ernzerhof (PBE) [12] for the exchange-correlation term. The Kohn-Sham (KS) equations are solved using the self-consistent method, as implemented in the Vienna *ab initio* simulation package (VASP) [13]. Projected augmented wave method [14] is applied to describe the electron-ion potential and a kinetic energy cutoff of 350 eV is selected for the plane wave expansion. We used $8 \times 8 \times 8$ and $8 \times 8 \times 1$ k-point grid for the first Brillouin zone according to the Monkhorst-Pack scheme [15] for the bulk and interface. All atoms in the enlarged supercell are allowed to relax without imposing any symmetry constraint. The forces are calculated using the Hellmann-Feymann procedure and geometries are optimized using the conjugated gradient (CG) scheme. The system is relaxed until the root mean square criterion of 0.002 eV/Å of the atomic forces is reached. In order to minimize stress effects on the interface due to incommensurability of lattice parameters of Al_2O_3 and GaN, the supercell used in the calculations was formed by two unit cells of Al_2O_3 and three unit cells of GaN. The resulting cells were superposed in the crystallographic direction 001 forming the basis of the supercell.

The system was assembled for the interface region in the xy-plane and the end structure was replicated using the vectors lattice of Al_2O_3. The thickness of the layers of Al_2O_3 and GaN is approximately 16 and 18 Å. A vacuum region of 20 Å separates adjacent unit cells along the growing z direction. This ensures that the interfaces in neighboring cells will not interact along the growing direction.

We have examined two structural models for the GaN (0001)/α-Al_2O_3 (0001) (GaN/Al_2O_3) interface. The first one exhibits N atoms of GaN structure aligned with the O atoms of the Al_2O_3 structure, called N-terminated interface. In the second one the atoms Ga of the structure GaN bond with O atoms of Al_2O_3 denominated Ga-terminated interface. In both systems we begin the calculations with N (Ga) binding with O atoms, but after complete relaxation of atomic positions the bond formed is between N (Ga) with Al atoms. Our simulations of GaN/Al_2O_3 N (Ga)-terminated indicate strong surface chemical selectivity with Al atoms migrating to the surface and O atoms migrating in the bulk, creating surface Al capping.

The calculations of the cohesion energies were performed according to the following equation:

$$E_c = E_{[\text{int}]} - E_{[\text{GaN}]} - E_{[\text{Al}_2\text{O}_3]}, \quad (1)$$

where $E_{[\text{int}]}$ is the total energy of the interface, $E_{[\text{GaN}]}$ is the total energy of a GaN layer, and $E_{[\text{Al}_2\text{O}_3]}$ is the total energy of the Al_2O_3 layer. The results for cohesion energies are −3.82 eV (−2.64 eV) to the N-terminated (Ga-terminated) interface, where we conclude that the N-terminated interface is the more stable and these results show that the main influence to the interface stability is given by the polarity of the GaN layer. In the following, we describe only the results of the N-terminated interface.

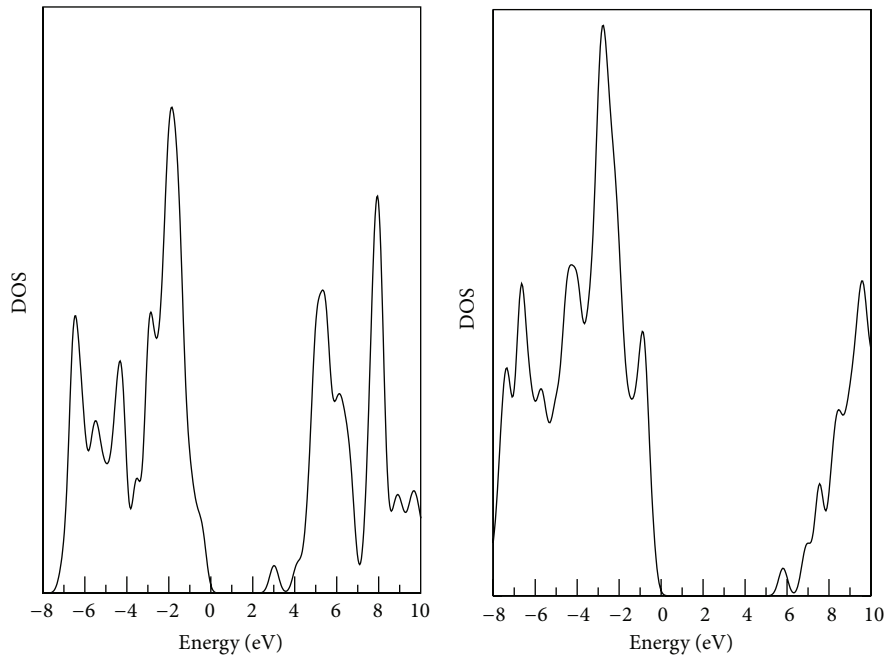

Figure 2: Total density of state of (a) GaN bulk and (b) Al_2O_3 bulk. The level Fermi is located in zero.

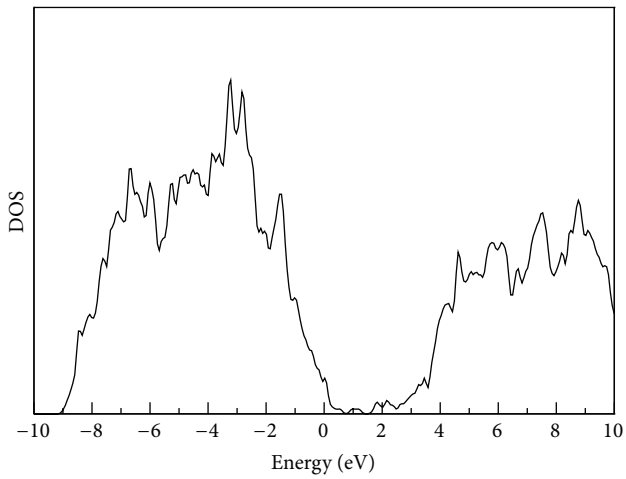

Figure 3: Total density of state of GaN/Al_2O_3 N-terminated interface. The level Fermi is located in zero.

Table 1: Some relevant interatomic distances and their variations (in parentheses) for the GaN/Al_2O_3 N-terminated interface. The numbers identifying the distances refer to Figure 1(b).

Distances (Å)	
1-2 = 1.897 (0.073)	17-18 = 1.951 (0.000)
2-3 = 1.842 (0.129)	18-19 = 1.901 (0.011)
3-4 = 1.787 (0.433)	19-20 = 2.013 (−0.108)
4-5 = 1.896 (−0.041)	20-21 = 1.871 (0.041)
5-6 = 1.976 (−0.005)	21-22 = 1.991 (−0.025)
6-7 = 1.874 (0.097)	22-23 = 1.862 (0.051)
7-8 = 1.870 (−0.015)	23-24 = 1.906 (0.000)
8-9 = 1.855 (0.116)	24-25 = 1.855 (0.058)
9-10 = 1.753 (0.219)	25-26 = 1.902 (0.003)
10-11 = 1.890 (0.082)	26-27 = 1.859 (0.053)
11-12 = 1.991 (0.231)	27-28 = 1.902 (0.004)
12-13 = 1.882 (−0.027)	28-29 = 1.861 (0.051)
13-14 = 1.885 (0.086)	29-30 = 1.895 (0.011)
14-15 = 1.865 (0.107)	30-31 = 1.869 (0.043)
15-16 = 1.761 (0.094)	31-32 = 1.881 (0.025)
16-17 = 1.881 (0.090)	32-33 = 1.897 (0.015)

3. Results and Discussion

The unit cell of unrelaxed and relaxed geometry of the GaN/Al_2O_3 N-terminated interface are shown in Figures 1(a) and 1(b), respectively. It can be noted by inspection of the figure that there is a modification after the structural relaxation, especially in the Al_2O_3 region. In Figure 1(b), some of the atoms are numbered in order to describe the relevant structural parameters. Directly comparing Figures 1(a) and 1(b) we notice that there have been changes mainly in the Al_2O_3 region especially near the interface region. Initially, the Al_2O_3 structure was terminated in oxygen, after was done total relaxation the Al_2O_3 terminated in aluminum. In Table 1, interatomic distances are listed for the GaN/Al_2O_3 N-terminated interface. The calculations show that vertical distances between Al and O atoms of Al_2O_3 are in good agreement with experimental and theoretical values reported in the literature [16–19], since the average of Al-O bonds calculated by us is 1.90 Å. Geometric data in interatomic distances of GaN are shown in Table 1. According to our

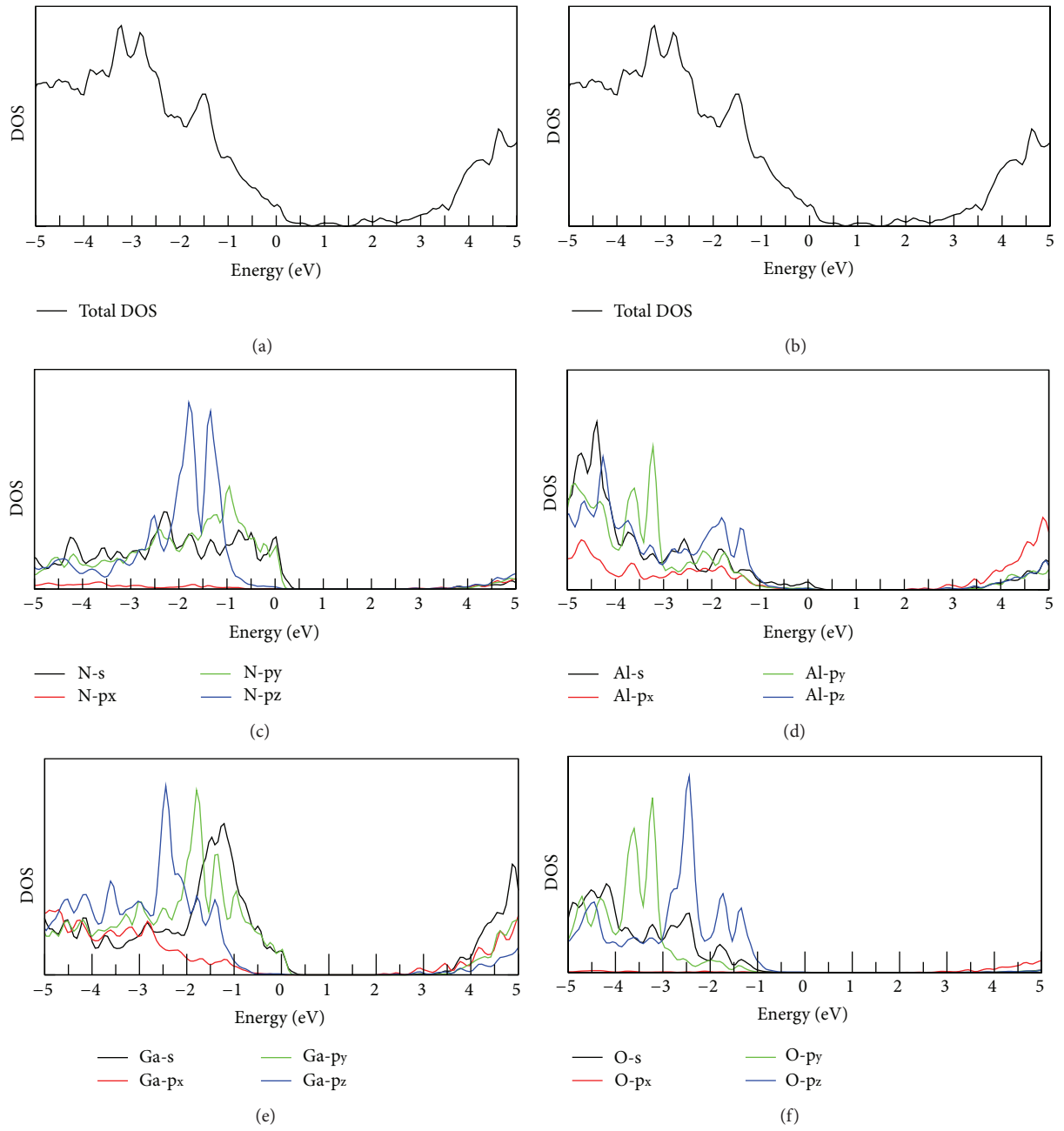

FIGURE 4: Projected density of states of N, Ga, Al, and O atoms located in the interface region. The Fermi level is located in zero.

calculations vertical distances between Ga and N atoms in each bilayer of the GaN region near to the interface are enlarged compared with GaN bulk distances. For instance, in Figure 1 the distance between atoms 18 and 19 is 1.90 Å, which is enlarged in 0.04 Å compared with the GaN bulk (1.86 Å). Similarly, the bond length between atoms 19 and 20 (2.01 Å) is stretched in 0.07 Å compared with the GaN bulk (1.94 Å). This stretching is due to stress imposed to the GaN region which leads to relaxations along the growing direction, where the GaN layers (near the interface) attempt to copy the equilibrium geometry of the Al_2O_3 region.

To verify that the methodology used in our calculations was appropriate, we first performed a study of the electronic properties in the GaN and Al_2O_3 bulk. Figures 2(a) and 2(b) show the electronic density of states (DOS) of GaN and α-Al_2O_3 bulk, respectively. The estimated energy gap of the GaN is of 3.42 eV, which is in accordance with the experimental energy gap [20]. The energy gap of Al_2O_3 bulk is 6.10 eV and this value is in good agreement with calculation in the literature [21].

Figure 3 exhibits the DOS of the N-terminated interface. We can notice that this interface is metallic, once the states intersect the Fermi level. The energy levels that appear around the Fermi level, from −1.5 eV and 0.3 eV, are contribution of the atoms located in the interface region. We infer that the metallization occur due to the stress that the system is

subjected to, as the lattice parameters of GaN were adjusted according to the lattice parameters of Al_2O_3, so rehybridizing of the GaN orbitals causes the semiconductor-metal transition.

The nature of these levels around the Fermi energy can be elucidated by looking the plot of the projected density of state (PDOS) on atomic states of atoms located at the four interface layers, that is, Ga and N atoms belonging to the first and the second layer of the GaN region, respectively. Also we plotted Al and O atoms of the first and the second layer of Al_2O_3 structure, respectively. Figure 4 shows the PDOS of the N, Ga, O, and Al atoms located in the interface region (see Figure 1). In Figures 4(a) and 4(b) we plotted the total DOS for comparison. We can see that the level above Fermi level, −0.5 eV to 0 eV, is a mixture of p_y orbital of the N and Ga atoms and a low contribution of s orbital of both N and Ga atoms (see Figures 4(c) and 4(d)).

The states that appear below Fermi energy, 0 to 0.27 eV, are contributions of s orbital of N atoms with low contribution of Ga atoms. The peak located in −1.5 eV is mainly due to contributions of the p_z orbital of the N atoms and p_y orbital of the Ga atoms. The Al atoms and O atoms, in the interface region, also contribute to the peak that appears at −1.5 eV below the Fermi level, with contribution of the p_z orbitals of Al and O atoms. The energy states that appear below (0.3 to 1.5 eV) the Fermi level are contribution of atoms that are not near the interface region and this contribution is mainly of Al and N atoms.

The results presented above allow us to infer that, from the PDOS plotted, there is a strong hybridization between −5.0 eV and −1.0 eV, as can be seen in Figure 4. The hybridization between the Al, O, Ga, and N orbitals suggests a covalent bond between the GaN layer and the Al_2O_3 substrate.

4. Conclusions

In this paper we show a study based on the DFT calculations of GaN/Al_2O_3 interface. The relaxed structure shows a change in the substrate Al_2O_3; initially the N (Ga) atoms bind to the O atom of sapphire; after optimizing, the N (Ga) atom binds to Al atom. This study aims to analyze the stability of this interface due to the fact that in general GaN is grown in Al_2O_3 substrate. Our calculations show that the N-terminated interface is more stable than the Ga-terminated. The interface presents allowed electronic states at the Fermi energy, leading to metallic states. The electronic properties of the GaN/Al_2O_3 N-terminated interface show that the strong hybridization that exists between the atoms in the interface region indicates that these atoms interact via covalent bond.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

Acknowledgments

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