



Fast-track communication

Tuning electronic properties of fully hydrogenated AlN nanosheets by external electric field: A van der Waals density functional study



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ABSTRACT

In this paper, the structural and electronic properties of two dimensional (2D) fully hydrogenated AlN nanosheets have been investigated by density functional theory computations with van der Waals (vdW) correction. The results demonstrate that there exists strong hydrogen bonding between the nanosheets. Especially, fully hydrogenated AlN monolayer and bilayer nanosheets both have an indirect band gap, irrespective of stacking pattern and thickness. The band gap of fully hydrogenated AlN monolayer and bilayer can be flexibly reduced by applying an external electronic field (*E*-field), resulting in a semiconductor → metal transition. The results provide many useful insights for the wide applications of AlN nanosheets in electronics and optoelectronics.

1. Introduction

The discovery of graphene among mechanically exfoliated graphite sheets and its unusual electronic properties in 2004 have led to an extraordinary amount of interest from both academia and industry [1]. The successful isolation of this two-dimensional (2D) crystal wholly refreshed our minds and brought us a new revolution to material science due to its extraordinary structural and electronic properties as well as promising applications in nanoelectronics [2–4]. The impressive progress in graphene research has motivated scientists to explore other 2D atomic based materials, including BN [5,6], GaN [7], germanane, [8] and MoS₂ [9]. Among them, AlN nanosheet has become a hotly pursued system as it shares the same honeycomb lattice structure as graphene, which has aroused extensive research interest due to its many intriguing properties such as high chemical stabilities, excellent mechanical properties and high thermal conductivity [10,11].

However, at present, some interesting issues still need to be addressed for this novel material. Unlike in its bulk structure, Al and N atoms on the surface of as-synthesized AlN nanosheets are arranged in planar 3-fold coordination instead of the bulk-like tetrahedral configuration. Zhang et al. predicted that AlN nanosheet semi-decorated with hydrogen and fluorine atoms can be a direct or an indirect semiconductor and exhibit completely distinct properties from its pristine forms [12]. The controllable band gap engineering of semiconductors is always highly desirable for a wide range of energy and sensing applications. In addition, Ding et al. reported that the band gap

of silicene/GaS nanosheets can be modulated by strain and an external electric field [13]. Can we also efficiently engineer the electronic properties of fully hydrogenated AlN nanosheets using some feasible approach?

Therefore, in this paper, the atomic structural and electronic properties of fully AlN nanosheets (H-AlN-H) are extensively carried out by density functional theory (DFT) calculations with vdW corrections. These studies provide us a deep understanding of the novel properties of hydrogenated AlN nanosheets, which is essential to employ them as building blocks for future nanodevices. Our computations have revealed that there is strong hydrogen bonding between H-AlN-H nanosheets. Especially, the electronic properties of H-AlN-H nanosheets layers can be efficiently engineered by applying an experimentally feasible external electric field (*E*-field).

2. Computational methods

The simulation is calculated by first-principles DFT, which is provided by DMOL³ [14–16]. The generalized gradient approximation (GGA) with the Perdew-Burke-Ernzerhof scheme (PBE) [17] is employed to optimize geometrical structures and calculate properties. The all-electron relativistic Kohn-Sham wave functions are expanded in the local atomic orbital basis set for DMOL³ [14]. In order to take into account the contributions of the van der Waals (vdW) interactions between layers, the DFT-D (D stands for dispersion) approach within the Grimme scheme is adopted for the vdW correction [18]. This method has been successfully applied in previous studies of the

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interaction between silicene on MoS₂ and benzene on Cu (100) surfaces [19]. Pseudopotentials with $3s^2 3p^1$, $2s^2 2p^3$, and $1s^1$ valence electron configurations are used for Al, N, and H atoms, respectively. Similar functional have been successfully used to study the structural and electronic properties of water, Si and Cu nanowires [20,21]. The nearest distance between nanosheets in neighboring cells is greater than 15 Å to ensure no interactions. For geometry optimization, both the cell and the atomic positions are allowed to fully relax. The Brillouin zone is sampled by $6 \times 6 \times 1 (10 \times 10 \times 1)$ k -points for all structures in the geometry optimization (electronic) calculations and the real space global cutoff radius is set to be 4.8 Å [22], which brings out the convergence tolerance of energy of 1.0×10^{-5} Ha (1 Ha=27.2114 eV), maximum force of 0.002 Ha/Å, and maximum displacement of 0.005 Å. Increasing the k -points mesh to $8 \times 8 \times 1$ for all structures in the geometry optimization does not greatly change the calculated quantities.

The electronic distributions of AlN nanosheet are carried out by Mulliken charge analysis, which is performed using a projection of a Linear Combination of Atomic Orbitals (LCAO) basis and to specify quantities such as atomic charge, bond population, charge transfer etc. LCAO supplies better information regarding the localization of the electrons in different atomic layers than a plane wave basis set does [23]. The obtained relative value of the charge e , but not the absolute magnitude, displays a high degree of sensitivity to the atomic basis set and a relative distribution of charge [24,25].

3. Results and discussion

The AlN nanosheets are constructed from the bulk phase. We begin our study with AlN hexagonal wurtzite (WZ) structure with $P63mc$ space group. The accuracy of our calculation procedure is also tested using pristine monolayer AlN nanosheet. A $4 \times 4 \times 1$ supercell of monolayer AlN nanosheet containing 32 atoms is constructed. Each N atom has three covalent bonds with the three adjacent Al atoms and two residual electrons per every N atom form a lone pair distributed perpendicularly to the sheet's plane such that all orbitals in AlN nanosheet exhibit a sp^2 -hybridization. The optimized lattice constant of 3.112 Å and bond length of Al–N of 1.797 Å are in good agreement with theoretical value of 3.121 Å and 1.808 Å, respectively [26,27].

A H-AlN-H bilayer can be constructed by pairing two H-AlN-H monolayers together. To determine the most stable configuration of H-AlN-H bilayer, we have performed a set of lateral shifts of H-AlN-H monolayer to the basal plane of the other monolayer and finally obtained 12 initial configurations to find out the optimal stacking manners. In detail, the upper H-AlN-H monolayer is firstly fixed. Then the other H-AlN-H supercell is moved along x -axis or y -axis. Thus, three representative stacking patterns are formed: Top structure (Al atoms situated directly above Al atoms, short for T_{Al} and N atoms situated directly above Al atoms short for T_N); Hollow structure (N atoms placed at the hollow sites of the N-Al-N hexagonal rings, short for H_N and Al atoms placed at the hollow sites of the N-Al-N hexagonal rings, short for H_{Al}); Bridge structure (N atoms located at the top of the mid-points of Al and N, short for B_N and Al atoms located at the top of the mid-points of Al and N, short for B_{Al}) are considered, which are shown in Fig. 1 a–f. In addition, the location of Al atom and N atom are exchanged. Thus, about $6 \times 2 = 12$ configurations are constructed as the initial stacking manners.

We have explored the effects of stacking pattern on the electronic properties of H-AlN-H layers. The band structures of the other eleven metastable configurations of H-AlN-H bilayer are also calculated. According to our computations, the structural parameters and E_g values for different patterns are similar, which are in agreement with the silicene - silicon [28] and silicene - MoS₂ [29] heterostructures. Thus, in the following, we only consider the most stable configuration in Fig. 1c, which has a characteristic that lower layer N atoms are placed at the hollow site of the upper layer N-Al-N hexagonal rings

(H_N). Meanwhile, DFT-D2 includes vdW contributions using a semi-empirical potential added to the total DFT energy [29,30]. With vdW, we have included the contribution of the dispersion forces in the whole system [31], while without vdW, dispersion forces have been excluded completely from the total energy.

In the bilayer system, the average intraplanar bond length d_{Al-N} is 1.92 Å. The Al and N atoms become sp^3 hybridized with H atoms bonded, which distorts the planar geometry forming a zigzag configuration. The optimized Al–H bond lengths (1.556 Å) and N–H bond lengths (1.032 Å) indicate the formation of strong chemical bonds between hydrogen and Al, N atoms [32]. The atomic charge transfers in H-AlN-H monolayer are analyzed by the Mulliken charge analysis [33–35]. The results indicate that the same atoms are equivalent and $e_N = -1.340 e$, $e_{Al} = 1.252 e$. Meanwhile, H atoms adsorbed on Al and N atoms are carrying charges of $-0.118 e$ and $0.206 e$, respectively. The interlayer distance d_0 (2.02 Å) means the nearest distance between bilayer H-AlN-H nanosheets, which is a typical distance for chemisorption [31].

In addition, the DFT-D method predicts a rather pronounced binding energy of 210 meV/unit cell. As a comparison, in previous studies, the binding energies of graphene bilayer, graphane bilayer, graphane/fluorographene bilayer, and germanane bilayer are 132, 66, 86, and 260 meV/unit cell, respectively [9]. Therefore, the interlayer coupling between H-AlN-H bilayer is rather strong, H-AlN-H bilayer will be highly stable once formed.

It was reported that the electronic properties of graphene related materials are modulated notably by weak interlayer interactions [28,29]. To reveal this effect on bilayer H-AlN-H nanosheets, the electronic structure is shown in Fig. 2. The bilayer H-AlN-H nanosheets is a nonmagnetic semiconductor with the indirect band gap (E_g) of 2.95 eV, which is 0.73 eV lower than the fully hydrogenated monolayer H-AlN-H. The slight energy level splitting in both the conduction and valence bands can be observed in the band structure of H-AlN-H bilayer, which removes the 2-fold degeneracy of VBM and CBM and decreases E_g correspondingly.

According to the Mulliken charge analysis, there is no charge transfer between the two monolayers. In contrast, induced by the interlayer coupling, an interlayer charge redistribution occurs in both monolayers, which should be responsible for the energy level splitting. The Mulliken charge analysis of H-AlN-H bilayer results indicate that the same atoms are equivalent and $e_N = -1.362 e$, $e_{Al} = 1.220 e$. Meanwhile, the Mulliken charge of H atom on Al atom is $-0.094 e$, while H atom on N atom is $0.235 e$. Moreover, since there is no spontaneous interlayer polarization between two monolayers, the energy levels of two monolayers are not separated from each other, and VBM and CBM are contributed equally by two monolayers [9].

In order to deeply evaluate the states near the E_F , the partial density of states (PDOS) of H-AlN-H bilayer are plotted in Fig. 2. It is found that the states of H-AlN-H bilayer near the E_F are mainly dominated by the bands of H atom, denoting that the electronic and transport behaviors of the structure are mainly affected after being fully hydrogenated. Moreover, in order to gain more insights into the electronic structure of H-AlN-H bilayer, the corresponding charge density isosurfaces of the lowest unoccupied molecular orbital (LUMO) and the highest occupied molecular orbital (HOMO) at Gamma point have been explored, where E_g of this system is determined by the two subbands. LUMO orbitals are primarily localized on the N atoms of the upper layer, while for HOMO orbitals, the charge densities are homogeneously distribute on H atoms of the lower layer, which are corresponding to our previous PDOS results.

Next we have studied the influences of an external E -field on the electronic properties of the H-AlN-H monolayer and bilayer. The external E -field is a powerful tool to achieve tunable properties in nanostructures. Recent theoretical studies have demonstrated that a band gap can be opened in the band structure of silicene on ultrathin silicon nanosheets by applying an external E -field [28]. Li et al. have

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