

Theoretical prediction of a novel aluminum nitride nanostructure: Atomistic exposure



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ABSTRACT

Aluminum nitride has significant prospect as a kind of ceramic material in applications such as semiconductors, sensors and other electronic devices. In this work, a novel AlN nanostructure is reported in terms of the optimized atomic structure, energetics, phonon dispersions and electronic structures employing the state-of-the-art Density functional theory (DFT). The interesting propeller-shaped AlN nanowire structure is determined with its detailed bond lengths and bond angles identified. In this structure, the orbital hybridization of Al and N atoms with coordination number of three is sp², and hybridization of Al and N atoms with coordination number of four and five are sp³ and sp³d, respectively. The binding energy and work function of the novel AlN nanostructure are −4.855 eV and −5.326 eV, respectively. The charge distribution inside the novel structure has also been explored through the differential charge density and the Bader charge analysis. The nanostructure has a band gap of 2.5 eV with its deep electronic structure revealed. This theoretical study proposes a new type of AlN nanowire and will make guidance for experimentalists to design novel III-V group ceramic nanostructures for semiconductor or other functional applications.

1. Introduction

In these years, the ceramic nanomaterials have drawn more and more attentions of materials scientists due to their surface or interfacial effects, quantum size effects as well as excellent electrical, mechanical or optical properties [1]. With the development of this field, various nanotubes, nanowires, nanosheets and other kinds of nanostructures are booming fast. In the early 1990s, the carbon nanotubes were first observed in experiments [2]. Since then, the detailed single-walled carbon nanotubes [3,4] and the multi-walled carbon nanotubes [5,6] had gradually been reported. Besides the system of group IV elements, the III-V group nanomaterials have also been widely studied [7–10] that are still being explored and investigated until now. Among them, the one-dimensional AlN nanostructures have peculiar morphologies and excellent properties and can be used in field emission and many other electronic devices [11]. These one-dimensional AlN nanomaterials, including nanotubes, nanowires and nanoribbons, etc. that have odd structures and properties, are worthy to be investigated continuously.

From experimental perspective, these AlN nanomaterials can be

synthesized by the direct nitridation [12,13], the catalyst-assisted growth [14,15], the DC arc discharge method [8,16], the vapour deposition process [17,18] and the template method [19,20]. As for the theoretical approach, some researchers employed the first-principles theory to investigate the performance of one-dimensional AlN nanomaterials to adsorb gases as materials for sensors and electronic devices [21–23]. There was also study to report the theoretical electronic and optical properties of AlN nanotubes by adsorbing metal atoms [24]. While in this study, we have utilized the Density functional theory to predict a new propeller-like AlN nanowire structure for the first time. The atomic bond lengths and bond angles, thermodynamic binding energy, lattice dynamic stability and the hybridization types of the novel AlN nanostructure are investigated systematically. The electronic structure of the novel nanowire is further unveiled besides the calculations of electronic charge transfer and differential charge density. It is proposed that this theoretical research would encourage and expedite the design and development of novel AlN-based nanomaterials.

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2. Theoretical methods

In establishing the atomic structure of AlN nanowire and predicting the energetics and electronic structure of the nanostructure, we have used the Density functional theory [25,26] method as implemented in Vienna Ab initio Simulation Package [27–29]. The projector augmented wave (PAW) [27] pseudopotentials were adopted. The generalized-gradient approximation (GGA) was employed in the scheme of Perdew–Burke–Ernzerhof (PBE) [30] to treat the exchange correlation energy. A plan-wave basis set with an energy cut-off of 520 eV was used. The K-points mesh of $15 \times 1 \times 1$ and $30 \times 1 \times 1$ were utilized in the stage of geometry optimizations and electronic structure calculations, respectively. The structural relaxations have been done by using conjugate gradient algorithm to relax all ions until the force between each atom was lower than 0.02 eV/\AA , and an electronic convergence criterion was 0.0001 eV . The density functional perturbation theory was adopted to calculate the phonon spectra for the novel AlN nanostructure by using phonopy [31]. The phonon property was calculated employing a $(8 \times 1 \times 1)$ supercell with $3 \times 1 \times 1$ k-point in VASP. The charge state of each atom has been calculated by the Bader charge analysis using the previous method [32–35].

3. Results and discussion

Firstly, a small Al_4N_4 cluster can be extracted from the Wurtzite AlN supercell. After geometry optimization, this small cluster would relax and become a cage-like Al_4N_4 cluster. In Fig. 1, we mark the numbers of one to six on the cage-like Al_4N_4 cluster. Then, three extra nitrogen atoms were added and bonded with each marked aluminum atom (i.e., No. 1, 2 and 3) respectively. In the same way, three extra aluminum atoms were added and bonded with each marked nitrogen atom (i.e., No. 4, 5 and 6) respectively. After the structural relaxation, a novel propeller-like Al_7N_7 nano-cluster is formed. Actually, we find that this interesting Al_7N_7 cluster is the unit cell of a novel nanowire structure, which is shown in Fig. 2. This novel AlN nanostructure has periodicity on the X-axis and can be theoretically extended to obtain an illimitable nanowire. The main view and side view of the unit cell can be seen in Fig. 2(a) and (b), and the AlN nanowire structure is shown in Fig. 2(c). Thermodynamically, the free energy of the nanowire unit cell is calculated to be -92.302 eV . In addition, in order to determine whether the novel AlN nanostructure is stable in lattice dynamics, we have also studied its phonon spectra. The calculated phonon spectra of the novel structure is shown in Fig. 3. No imaginary frequency mode is found in this structure. Therefore, the dynamic stability of the novel AlN nanostructure is also good, which is significant for the future experimental

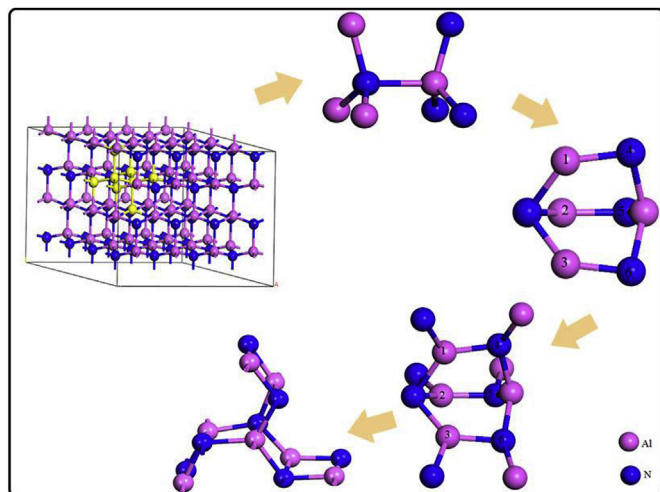


Fig. 1. Illustration for the stepwise formation of the Al_7N_7 nanocluster.

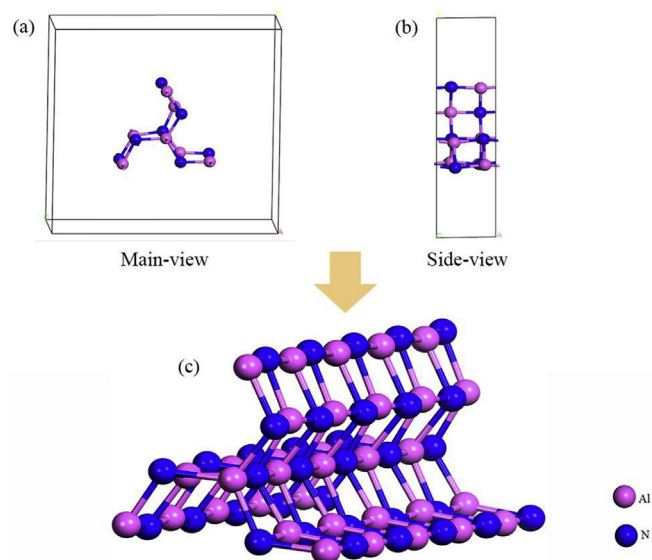


Fig. 2. (a) Main view of the optimized structure of nanowire unit cell, (b) Side view of the nanowire unit cell, (c) Demonstration of the novel AlN nanowire structure.

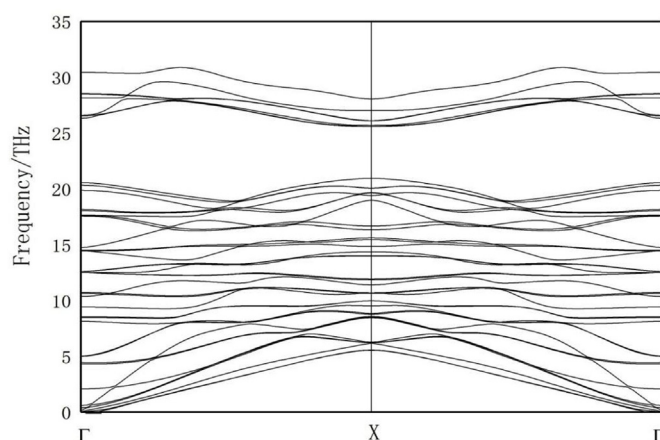


Fig. 3. Phonon spectra of the novel AlN nanowire structure.

synthesis.

This propeller-shaped structure is fascinating, which stimulated us to reveal its detailed structural information of bond lengths and bond angles. The propeller-like structure can be considered to have three “blades”, each of which consists of two quadrilaterals, and the three blades are connected by the same Al–N bond to form the “propeller”. Fig. 4 shows the detailed bond lengths and bond angles of the new structure. The bond lengths of the structure can be divided into two groups: the “longitudinal” and “transversal”. In detail, there are three further kinds of “longitudinal” Al–N bond lengths. The length of the Al–N bond that connects three blades is the shortest, which is 1.819 \AA . The lengths of the outward Al–N bonds are 1.836 \AA and 1.828 \AA , respectively. There are also three types of “transversal” bond lengths. The Al atom that on the shortest longitudinal Al–N bond is linked with three “transversal” bonds having the length of 2.03 \AA . Similarly, the length of three bonds linked by that N atom is 1.96 \AA . The outward transversal Al–N bonds have the length of 1.94 \AA . The bond angles information is shown in Fig. 4(c). There are two bonding angles for the “blades”: the bonding angle of Al–N–Al is 118.29° , and the bonding angle of N–Al–N is 128.51° . In the outermost quadrilateral of each blade, the angles of N–Al–N and Al–N–Al are 95° and 85° respectively. In the inner quadrilateral of each blade, the angles of N–Al–N is 91° and that of Al–N–Al

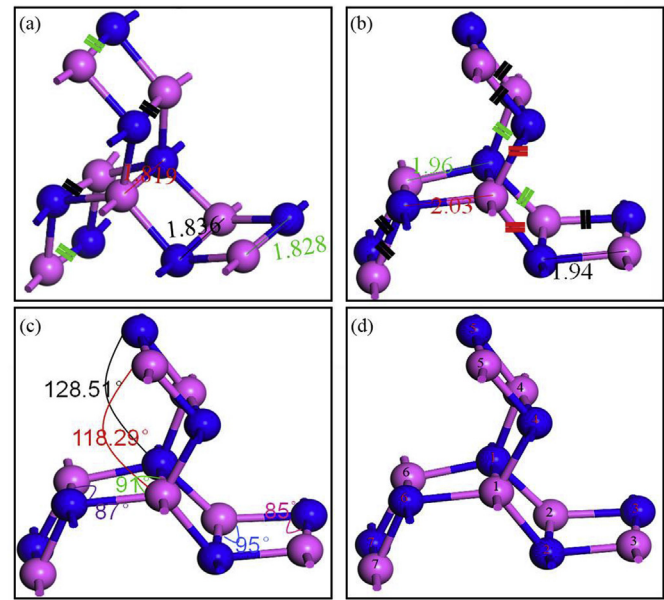


Fig. 4. (a) (b) The bond lengths of the novel AlN nanostructure, (c) The bond angles of the structure, (d) The numbering of every atom in the structure for convenience of investigation.

Table 1
Coordination numbers in the novel AlN nanostructure.

Atom	Coordination number
1(Al/N)	5
2,4,6(Al/N)	4
3,5,7(Al/N)	3

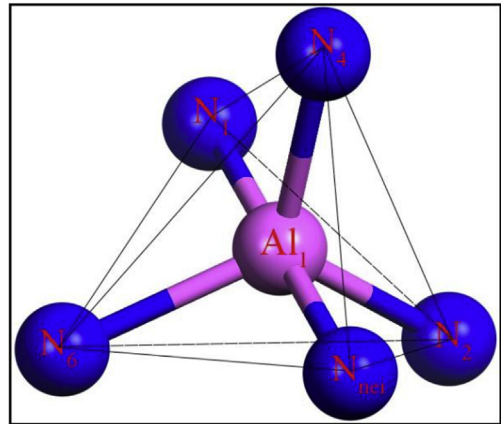


Fig. 5. The local structure with coordination number of five.

Table 2
The free energy (E, eV), binding energy (E_b, eV), magnetic moment (M) and work function (Φ, eV) of the novel AlN nanowire structure.

System	E (eV)	E _b (eV)	M (μ)	Φ (eV)
The novel AlN nanowire structure	−92.302	−4.855	0	−5.326

is 87°. These data of bond lengths and bond angles lay a solid foundation for the following coordination and hybridization studies.

In order to better understand the coordination and hybridization circumstance in this novel structure, we label every atom with Arabic numbers, which is shown in Fig. 4(d). There are three kinds of

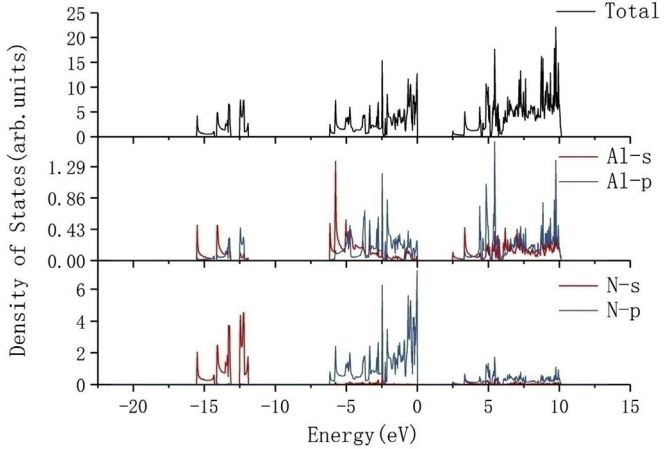


Fig. 6. The total and partial electronic density of states of the novel AlN nanowire structure. The Fermi level is set at zero.

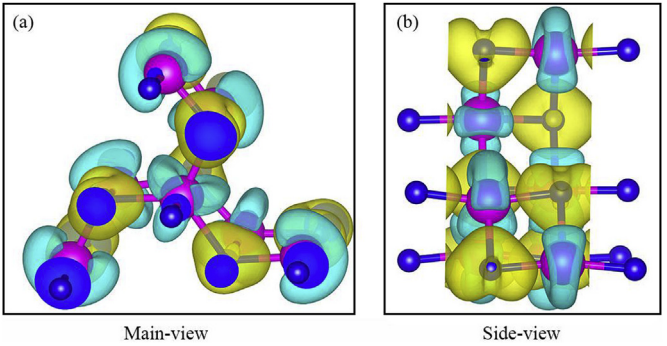


Fig. 7. The isosurface of the differential charge density (a) Main view (b) Side view of AlN nanostructure (yellow and cyan represent charge accumulation and charge depletion, respectively; isovalue = 0.01 eV/Å³). (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

Table 3
Charge states of Al and N atoms in the AlN nanowire unit cell, the atomic numbering is in accordance with those in Fig. 4d.

Al	1	2	3	4	5	6	7
Charge state (e [−])	+2.38	+2.32	+2.24	+2.35	+2.25	+2.33	+2.25
N	1	2	3	4	5	6	7
Charge state (e [−])	−2.42	−2.34	−2.25	−2.34	−2.25	−2.32	−2.24

coordination numbers (shown in Table 1) in the novel structure. The coordination number of No. 3, 5, and 7 Al/N atoms is three, and that of No. 2, 4, 6 Al/N atoms is four. The No. 1 Al/N atoms connecting three blades have the largest coordination number of five. The Al and N atoms with coordination number of three are hybridized by one 3s and two 3p and form three sp² hybrid orbitals, whose space configuration is planar. The atoms of Al and N with coordination number of four form a small AlN₄ or NAl₄ with tetrahedron configuration. Al atoms have empty p orbitals, N atoms have a full sp orbital and three semi-full sp orbitals. For this bonding of N and Al, the sp³ hybridization is formed. For the case with the coordination number of five, we have made a sketch as shown in Fig. 5. As is explained above, the Al₁, N₁, N₂, N₄, N₆ belong to a same unit cell. The N_{nei} represents the nitrogen atom in the neighbouring unit cell. All these atoms compose a hexahedron, in which the central Al₁ and N are sp³d hybridized.

The binding energy of the novel AlN nanostructure is −4.855 eV, which can illustrate the tightness between Al and N atoms. The calculation is based on the following formula:

$$E_b = [E(\text{AlN})_n - nE(\text{Al}) - nE(\text{N})] / 2n \quad (1)$$

where $E(\text{AlN})_n$ is the total energy of the AlN nanowire unit cell, while $E(\text{Al})$ and $E(\text{N})$ stand for the total energy of Al and N atom, respectively. Furthermore, the work function of the new structure is also calculated (seen in Table 2). The formula is:

$$\Phi = V(\infty) - E_F \quad (2)$$

where Φ is the work function, $V(\infty)$ and E_F are the electrostatic potential in vacuum and the Fermi energy of the system, respectively. The calculated value of the work function is -5.326 eV. We have also calculated the magnetic moment of this structure and found that the pure system is a nonmagnetic material.

After revealing the atomic structure, we also studied the electronic structure of the novel nanowire. Fig. 6 shows the density of states of the new material. This AlN nanostructure is a kind of semiconducting material with a band gap of 2.5 eV. The total density of states nearby the valence band maximum are mainly contributed by the p state of nitrogen, and those nearby the conduction band minimum are mainly contributed by the s state of aluminum. The good overlapping between the PDOS of Al and N indicates that the bonding between them is strong. We further analyzed the novel nanowire structure from the differential charge density perspective, as shown in Fig. 7. It is obvious that the electron density around N is increased while that of Al is decreased. The specific charge distribution can be got from the Bader calculations and the result is shown in Table 3. The maximum electron loss of is $2.38 e^-$ (Al_1 atom) and the N_1 atom gets the most electrons, which is $2.42 e^-$. Compared with Al_1 atom, the electron loss of outer Al atoms is smaller with the values of $2.32 e^-$, $2.35 e^-$ and $2.33 e^-$ for Al_2 , Al_4 and Al_6 respectively. The outmost Al_3 , Al_5 and Al_7 atoms have the least electron loss. This matches very well with the above coordination analysis.

Summary

This theoretical work reports a new type of AlN nanowire structure obtained by ab initio thermodynamic and lattice dynamical calculations. We have systematically unveiled the atomic and electronic structures of the novel AlN nanostructure. This propeller-like AlN nanowire structure has three kinds of longitudinal Al–N bond lengths and three kinds of transversal Al–N bond lengths. The orbital hybridization type between Al and N is closely related with the atomic coordination number. The sp^2 , sp^3 and sp^3d hybridizations correspond to the three types of coordination number of three, four and five respectively. The charge states of Al and N atoms at the junction of three “blades” is the largest. The electronic and magnetic calculations help to find that this novel AlN nanowire structure is a nonmagnetic semiconducting material. We hope this work of discovery will stimulate more research of novel AlN nanomaterials and provide theoretical guidance for experimentalists.

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