# Electronic and structural properties of N-vacancy in AlN nanowires: A first-principles study*

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The stability and electronic structures of AlN nanowires with and without N-vacancy are investigated using first-principles calculations. We find that there is an inverse correlation between formation energy and diameter in ideal AlN nanowires. After calculating the formation energies of N-vacancy at different sites in AlN nanowires with different diameters, we find that the N-vacancy prefers to stay at the surface of the nanowires and it is easier to fabricate them under Al-rich conditions. Through studying the electronic properties of AlN nanowires with N-vacancies, we further find that there are two isolated bands in the deep part of the band gap, one of them is fully occupied and the other is half occupied. The charge density indicates that the half-fully occupied band arises from the Al at the surface, and this atom becomes an active centre.

**Keywords:** AlN nanowires, vacancy, first-principles

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## 1. Introduction

Nanotechnology is impacting almost all aspects of science and technology, owing to the unique properties of nanostructure materials, which result in potential applications in a wide area ranging from semiconductor devices to drug delivery systems. Recently, AlN nanowires have attracted attention due to their fascinating properties,[1−5] such as a large band gap and low electron affinity, and worthy applications in wireless communication and optoelectronics technology in the ultraviolet and visible regions.[6,7] So far, significant efforts have been devoted to fabricating high-quality nanowires by employing different techniques.[8−11] A great deal of work has been done to investigate the basic properties of AlN nanotubes and nanowires.[1,3,12,13] Wu *et al.*[6,14] calculated the electronic structure of an AlN nanowire and proposed a possible phase transition during the growth of the AlN nanowire, Rezoualin *et al.*[12] reported on *ab initio* studies of the confinement and surface effects in AlN nanowires. However, all these studies focused mainly on ideal AlN nanowires and few papers gave an account of AlN nanowires with defects. Moreover, it has been found that defects in ZnO[15,16] and GaN[17] nanowires affect their properties, and influence conductivity performance and photo catalytic activity, so we may expect that defects in an AlN nanowire would also have a large effect on its properties. However, defects in AlN nanowires are still poorly understood. In this paper, we focus on the N-vacancy ($V_{\rm N}$) which is the most stable native defect in AlN bulk[18,19] and is almost inevitable due to the thermal vibration or chemical composition deviating from the normal proportion in the process of fabricating.

In this work, we study the atomic structures, formation energies, and electronic structures of $V_N$ in nonpassivated AlN nanowires with different diameters. We find an inverse relationship between formation energy and diameter in an ideal AlN nanowire. The $V_{\rm N}$ is more likely to stay at the surface and generates two defect levels in the band gap, one of which is fully occupied and the other is half occupied.

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## 2. Calculation method

In this study, all the structural relaxations and energy calculations are performed using the density functional theory that incorporates exchange and correlation effects within the generalized gradient approximation (GGA).[20] We use the PW91 functional for GGA and a plane-wave basis set with the projector augmented wave method[21] as implemented in the Vienna *ab initio* simulation package (VASP).[22] The cutoff energy for the basis function is set at 500 eV and the atomic structure is relaxed until the force acting on each atom is less than 0.03 eV/Å (1 Å = 0.1 nm). The Monkhorst–Pack sampling scheme with a $1\times1\times3$ $k$-point mesh is chosen in our calculations.

Figure 1 shows the atomic configurations, all the nanowires are generally along the polar [0001] orientation, are accompanied by six {100} lateral facets, and have diameters from 3.65 Å to 15.63 Å. We use our optimized lattice parameters for bulk AlN: $a = b = 3.125$ Å, and $c = 5.007$ Å, which are very close to the experimental values: $a = b = 3.112$ Å, and $c = 4.982$ Å.[19] A 10-Å vacuum region is equipped to eliminate the interaction between neighbouring nanowires.

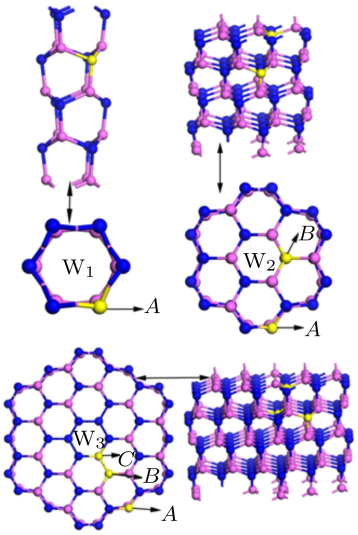



**Fig. 1.** Side and top views of AlN nanowires ($W_1$, $W_2$ and $W_3$). The black and grey atoms represent N and Al atoms respectively, and the N vacancy sites are denoted by $A$, $B$, and $C$, corresponding to the surface, subsurface, and interior respectively.

The formation energy of the AlN nanowire and the defect are defined as follows:

$$E_{\rm f}^{n\rm w} = E_{\rm tot}^{n\rm w} - n_{\rm N}\mu_{\rm N} - n_{\rm Al}\mu_{\rm Al}, \quad (1)$$

$$E_{\rm f}^{\rm def} = E_{\rm tot}^{\rm def} - E_{\rm tot}^{n\rm w} + \mu_{\rm N}, \quad (2)$$

where $E_{\rm f}^{n\rm w}$ is the formation energy of the AlN nanowire without a defect, and $E_{\rm f}^{\rm def}$ is the formation energy of $V_{\rm N}$ in an AlN nanowire; $E_{\rm tot}^{n\rm w}$ and $E_{\rm tot}^{\rm def}$ are the total energies of ideal and defect structures, respectively; $n_{\rm N}$ and $n_{\rm Al}$ are the numbers of N and Al atoms respectively; $\mu_{\rm N}$ and $\mu_{\rm Al}$ represents the chemical potentials of N and Al, respectively.

## 3. Results and discussion

### 3.1. Ideal AlN nanowires

Before investigating the defects of AlN nanowires, we studied the structural properties of the ideal ones and found that their electronic properties are greatly determined by the dangling bonds at the lateral facets. Because of non-passivation, the charge transfers from the dangling bond of surface Al to N always occur, which induces bending and contraction of the surface Al–N bonds after relaxation. The bending angles obtained for the three models in Fig. 1 are about 7° and the bonds are contracted by $\sim 6\%$. These data are consistent with Ye *et al.*'s report of (100) surface.[7] The atomic motions in this relaxation further lead to the separation between positive and negative charge centres in the radial direction. A dipole perpendicular to the lateral surface is present, which influences the stability and transport properties of AlN nanowires. Similar problems for ZnO have been discussed in detail.[15,23]

The formation energies of these nanowires without defects are revealed in Fig. 2. It is obvious that the formation energy decreases from 2.0 eV/AlN to 0.7 eV/AlN with an increase in diameter, which fits well with the data reported by Wu *et al.*[6] This decrease originates mainly from the decrease of the relative atom number at the surface rather than any other physical mechanism, and it approaches zero when the diameter is large enough. To probe the possible physical effects from the change of diameter, the contribution from relative atom number at surface is separated in the insert of Fig. 2, in which the formation energy is normalized by setting the largest value to be 1. From the figure, we can clearly see that the smaller the nanowire, the stronger the binding among atoms is, which can also be obtained by the band gap change trend, i.e. the smaller nanowire has a larger band gap.[24] Moreover, it can be seen that the curve of the relative atom number at the surface has the same trend as the curve of the formation energy, which

means that the formation energy is highly dependent on the surface, suggesting that the surface effect plays a dominant role in these nanowires.

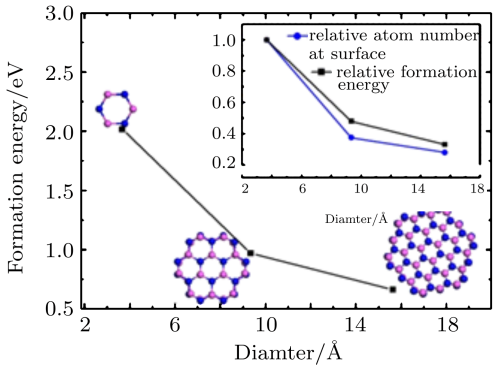



**Fig. 2.** Formation energies of AlN nanowires with various diameters. The insert shows the relative atom number at the surface and the relative formation energy per atom pair with respect to diameter.

## 3.2. N vacacy ($V_N$) in AlN nanowire

Special attention is paid to the $V_N$ in AlN nanowire because it is a common native defect in AlN bulk.[25,26] Its stability in nanowires and its effect on electronic structure are discussed here. The period of the defect models is doubled along $c$ orientation to avoid the interaction between neighbour defects. The removed N atom may be at the surface, subsurface or interior of the nanowire. The specific sites under consideration are denoted by $A$, $B$, $C$ as shown in Fig. 1.

The values of formation energy $V_N$ under different conditions are calculated by Eq. (2) and revealed in Fig. 3. The formation energies of $V_N$ under Al-rich conditions are much lower because N is lacking under these conditions. It is also obvious that the values of $V_N$ at the surface layer are more stable than those at the subsurface and interior of the nanowires. The values of formation energy $V_N$ at interior and subsurface are about 6 eV–7 eV, close to the values reported for bulk AlN,[26] while the values at the surface layer are smaller than 1 eV under Al-rich conditions, indicating that they easily occur at the surface. The origin of this is that the formation of $V_N$ at the surface layer involves breaking three Al–N bonds and four at the subsurface and interior. Another considerable factor is the surrounding atoms of $V_N$ at the surface layer, which can relax more freely. As shown in the insert of Fig. 3, the three nearest neighbour Al atoms obviously shift toward the vacancy centre, with an expansion of the Al–N bond being 0.5%–3.4%, and the total energy is decreased by this relaxation. The origin of this atomic relaxation can be found from electronic structure analysis. It is known that by removing an N atom from an ideal AlN nanowire produces Al dangling bonds and the unpaired electrons must redistribute to reach a more stable configuration, which is the intrinsic drive of atomic relaxation.

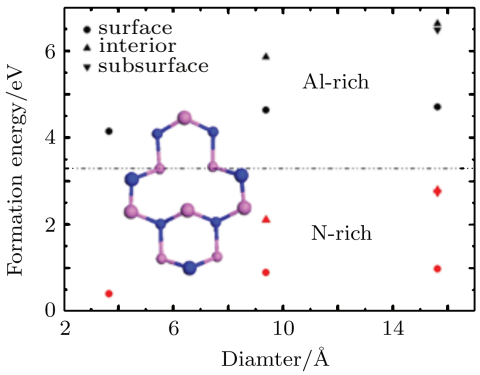



**Fig. 3.** Defect formation energies for the $V_N$ in AlN nanowires as a function of the diameter at N-rich and Al-rich conditions respectively. The insert performs the atom distribution around the nitrogen vacancy. The bigger atoms exhibit the surface atoms and the smaller are at the sublayer.

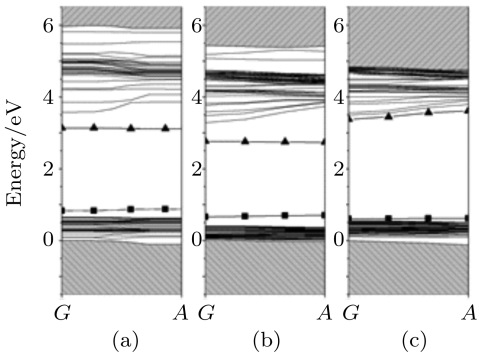



**Fig. 4.** Energy band structures of AlN nanowires with $V_N$ at (a) $W_2$ (site-$A$), (b) $W_3$ (site-$A$), and (c) $W_3$ (site-$B$). The grey shaded region corresponds to the bulk projected band structure. The lines without symbols in the band gap present the surface states of the defect surface, and the lines marked with squares and triangles denote the half occupied and occupied bands respectively.

The final energy band structures of an AlN nanowire with isolated $V_N$ at diferent sites are shown in Figs. 4(a)–4(c), corresponding to $V_N$ locating at site-A in nanowires $W_2$ and $W_3$, and site-B in nanowire $W_3$, respectively. The shaded grey regions in the lower and upper parts correspond to the valance and conduction bands of bulk AlN. The lines (without symbols) above the valence band maximum are from

the dangling bonds of surface N and the others below the conducion band mimimum are from the dangling bonds of surface Al. In addition, the two bands marked by symbols are related to $V_{\rm N}$. The Fermi level lies across the band marked by trigonal stars, so it is half occupied and the other one, marked by square stars, is fully occupied.

As for the $V_{\rm N}$ at the surface (see Figs. 4(a) and 4(b)), defect states are isolated from the surface states, while as for the $V_{\rm N}$ situated at the subsurface (see Fig. 4(c)), the defect states are not so isolated from the surface states. Moreover, the level marked by trigonals together with the states from surface Al dangling bonds in Fig. 4(c) shift upward and overlap with the bottom of the conduction band.

To find out the origin of the two bands related to $V_{\rm N}$, the corresponding charge density is plotted in Fig. 5. The partial charge density of the fully occupied band lies mainly between the surrounding three Al atoms, implying that a chemical bond is formed between them. The distance between the two Al atoms at the sublayer shrunk by 6.02%. The partial charge density of the half occupied band is located above the Al atom at surface, indicating that it is still a dangling bond and the Al atom becomes an active centre, as it is easy to release an electron. Therefore, the polarization and conductivity properties of AlN nanowires may be greatly influenced by it.

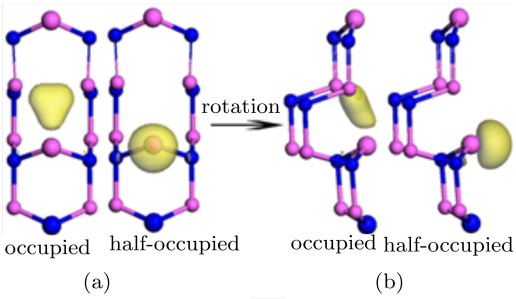



**Fig. 5.** Electron density distributions in the AlN nanowires with $V_{\rm N}$ for the lower vacancy state (fully-occupied) and higher vacancy state (half-occupied). The big and small atoms represent the sites at the surface and sublayer respectively.

## 4. Conclusions

In this paper, electronic and structural properties of defects in AlN nanowires with different diameters are explored by using the first-principles calculation method. Our theoretical study confirms that the formation energy of an ideal AlN nanowire is proportional to the inverse of the wire diameter, whereas the $V_{\rm N}$ in a nanowire is energetically preferred under the Al-rich conditions. In addition, it is found that the most stable location for $V_{\rm N}$ is on the edge of the nanowire. $V_{\rm N}$ induces two states in the band gap, i.e., the fully occupied single state located above the states from the dangling bonds of surface N, and the half-occupied state located below the states from the dangling bonds of surface Al. Furthermore, the corresponding charge density indicates that the half-fully occupied band is located above the Al atom at the surface, and this Al atom becomes an active centre.

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