Mechanical and electronic properties of 2D black phosphorene nanoribbons: A first-principles study

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Abstract. The mechanical and electronic properties of black phosphorene nanoribbons are studied using the first-principles calculations. The armchair black phosphorene nanoribbons (APNR) are obtained and the atomic reconstruction is found at the edge of the nanoribbons. In addition, the strain field is applied on the nanoribbons, and its stress-strain curve, Young's modulus, and Poisson's ratio are calculating by stretching APNR. It is found that the Young's modulus enhanced with the increase of nanoribbons width. It is significantly lower than the Young's modulus of monolayer black phosphorene. On the contrary, the Poisson's ratio hardly changes with the increase of nanoribbons width. Finally, it is found that the band gap of APNR decreases with the increase of nanoribbons width and increases monotonically with the increase of strain.

1. Introduction

Two-dimensional materials have drawn much attentions due to their special properties. They have strong size effect and large specific surface area. Moreover, monolayer or few-layer black phosphorene has important research value in sensors such as transistors [1], so black phosphorene has extraordinary research significance. Different from other two-dimensional materials, black phosphorene has a wrinkled honeycomb shape, which causes it to have special properties such as negative Poisson's ratio [2].

When the geometric size of the material reduces to the nanoscale, it tends to have some new characteristics that are not available in the macroscopic view. Therefore, the black phosphorene also has some characteristics after being cut into quasi-one-dimensional nanoribbons. The width-dependent magnetic properties of armchair black phosphorene nanoribbons by controlling the electron charge doping and the edge-to-edge magnetic coupling can be manipulated by charge doping because the transition from the antiferromagnetic to ferromagnetic state was achieved.[3] Cai[4] et al. performed numerical experiments of self-assembling a jammed black phosphorus ribbon on a fixed carbon nanotube. Xiao[5] et al. investigated the electronic structure and carrier mobility of monolayer black phosphorus nanoribbons (BPNRs). It indicates that BPNRs can be considered as a new kind of nanomaterial for applications in optoelectronics, nano-electronic devices owing to the intrinsic band gap and ultrahigh charge mobility.

At present, most of the researches on black phosphorene nanoribbons mainly focus on doping, adsorption, electronic structure and so on. Mainly studies are focus on the ideal 2D black phosphorene structures. Therefore, in this work, by using the first-principles method, the mechanical and electronic properties of black phosphorene nanoribbons are studied from both the atomic and electronic point of view. In addition, the finite-size dependence of tensile strain is investigated as well.
2. Model and calculation method
Ab initio (first-principles) calculations based on the density functional theory (DFT) are performed using the VASP code. We used the Perdew–Burke–Ernzerhof exchange-correlation functional, and the kinetic energy cut off for the plane wave basis set is chosen to be 400 eV. Atomic positions are relaxed and all the maximum Hellmann-Feynman force on any atom are less than $10^{-5}$eV Å$^{-1}$. In order to accurately describe the interaction between the nucleus and electrons, the valence electrons in this article are P 3s$^2$ and 3p$^3$.

The BP nanoribbons selected in this article are armchair black phosphorene nanoribbons (APNR). We can obtain APNR by cutting a monolayer black phosphorene (BP) along the direction of the armchair. The structure of BP is shown in Figure.1(a), and the black box in the figure is its single unit cell. We define the width $N$ of APNR to be 4 atoms as the unit width as shown in the Figure.1(b), so we can call APNR with different widths $N$ as $N$-APNR. The main object of the study is APNR with widths 3 to 7 because the widths 1 and 2 are too narrow. A vacuum layer with $l_v \geq 1.5$ nm thickness is introduced in the $x$ and $z$ directions respectively, the lattice coefficient $b$ in the $y$ direction is the same as that of BP, and the lattice coefficient in the $x$ direction is $a=N^*a_0+l_v$ ($a_0$ is the lattice coefficient in the $a$ direction of BP). As shown in Figure.1, the $x$ direction is the width direction of APNR, and the $y$ direction is the expansion direction of the nanoribbons. Because there are vacuum layers in both directions, the k points in the $x$ and $z$ directions are set to 1, and the k points in the optimization of the unit cell structure is set to $1\times25\times1$.

![Figure 1: Structure of (a) BP and (b) APNR from the top view and side view](image)

3. Results and discussion

3.1 The optimization structure of APNR
The optimized structure of APNR is shown in Figure.2.

![Figure 2: APNR structure after optimization from the (a) top view and (b) side view](image)

The structure of APNR has changed significantly after optimization. Firstly, it is shown on the atoms in the middle part of the structure. In order to maintain a more stable structure, it can be observed that the distance between atoms in the $z$ direction becomes larger, that is, the thickness of the nanoribbon is thicker, but the bond angle in the same plane does not change much. Secondly, the change appears on
the edge atoms, which are smaller in the $z$ direction relative to the atoms in the middle part, showing a tendency to shrink inward. In the $y$ direction, the distance between the atoms at the edge becomes larger, opening to both sides. In general, the undulations of the edge atoms have a smaller undulation angle in the $y$ direction, which is different from the wrinkled structure of the middle atoms, which tends to be flattened. We call this edge change the edge reconstruction, because the atomic coordination number at the edge of the nanoribbon is less, and the low-coordination edge P atoms significantly reduce the energy of the system through electron delocalization, making the system more stable. It forms additional $\pi$ bonds, and the condition for forming $\pi$ bonds is that the atoms are basically on the same plane. Under the action of the additional $\pi$ bonds, the edge of the nanoribbon reduces the degree of wrinkles and edge reconstruction occurs.

3.2 Mechanical properties of APNR

The mechanical properties are the focus of this study. After the nanoribbon structure relaxes, it is stretched in the expansion direction to apply the stretch to obtain the stress-strain curve of APNR. At the same time, the Young's modulus of APNR can be obtained by linear fitting in the linear region of the stress-strain curve.

Figure 3 is the stress-strain curve of APNR. We can find that the slope of the APNR curve increases as the width of the nanoribbon becomes wider, which indicates that as the width of APNR increases, its ability to resist deformation increases. Interestingly, when strain is applied to APNR up to 15%, the stress of APNR of all widths does not drop sharply, which means that its fracture strain is relatively large, and it can maintain a large fracture strain even when the width is narrow. This property is very similar to that of BP, it also has a high fracture strain, which is retained in APNR.

![Figure 3](image). The stress-strain curve of APNR with different width.

In addition, Figure 4(a) is the Young's modulus of APNR. By comparing the Young's modulus of APNR with different widths, it can be found that as the width of APNR becomes wider, its Young's modulus gradually increases and its growth rate is relatively large. At the same time, we calculated the Young's modulus of the BP as 12.149GPa. Comparing the Young's modulus of the overall APNR with it, it is found that the Young's modulus of APNR is much smaller than that of the BP. The width in the armchair direction is drastically reduced, so the ability of the material to resist deformation is reduced. As the width of APNR increases, eventually its Young's modulus will tend to BP.
Figure 4 (a) The Young's modulus of APNR and (b) Poisson's ratio of APNR

The Poisson's ratio is also the focus of this research. We calculated the Poisson's ratio of different widths through the definition of Poisson's ratio. As shown in Figure 4(b), the Poisson's ratios of APNR with widths of 3 to 7 are all distributed from 0.12 to 0.14. In general, the Poisson's ratio does not change much. Therefore, the width has less influence on APNR. While the Poisson's ratio of BP is 0.4\(^2\), it can be found that the Poisson's ratio of APNR is generally smaller than that of BP. We can explain by comparing the structure of BP and APNR. The main difference between APNR and BP structure is that there is edge reconstruction at the edge of APNR. These edges in the stretching direction are originally relatively flat structures, so these will not fully expand during stretching, resulting in smaller shrinkage.

3.3 Electrical properties of APNR

The electrical properties of APNR are also crucial. Before calculating APNR, we calculate the energy band structure of BP as shown in the Figure 5 to compare with APNR. From the energy band structure, it can be found that the Fermi line passes through the band gap and has a bandwidth of 0.916 eV, so black phosphorous is a semiconductor material with a band gap of 0.916 eV. The lowest point of the upper energy level and the highest point of the lower energy level correspond to the same abscissa. That is, the top of the valence band and the bottom of the conduction band are on the same abscissa, so the BP is a direct band gap.
We calculate the energy band structure of APNR, and Figure 6 corresponds to APNR with a width of 3 to 7 respectively. Compared with BP, it can be found that the top of the valence band and the bottom of the conduction band of APNR are not on the same abscissa, which indicates that APNR is an indirect band gap, which is completely different from BP. In terms of band gap value, we can measure the band gap of 3-APNR as 0.887 eV, which is very close to the band gap of BP. But 3-APNR is an indirect band gap, so the wave vector is different, and there is a change in momentum during the transition. In the direct band gap, they have the same momentum, so the electrons only change in energy during the transition process, and there is no change in momentum. In contrast, the electronic transition of BP is more likely to occur. On the other hand, as the APNR width increases, the corresponding band gaps are 0.887 eV, 0.689 eV, 0.517 eV, 0.468 eV and 0.443 eV, respectively. We can find that the band gap gradually decreases, which indicates that the width of APNR has a greater impact on the band gap. When the width reaches 6 and 7, the band gap of APNR is already less than 0.5 eV, and 0.5 eV is generally the dividing line between conductor and semiconductor. This indicates that when the width is large, the conductivity of APNR may change.

In order to study the influence of strain on the APNR band structure, we select 5-APNR for stretching.
and compression, and calculate its band structure. Figure 7 shows the band structure of 5-APNR after strain control. The band gaps corresponding to strain values of -4%, -1%, 1% and 4% are 0.450eV, 0.513eV, 0.553eV and 0.606eV, respectively. Compared with the original energy band structure of 5-APNR, the top of the valence band still appears at Γ point. In terms of band gap, the band gap of APNR will decrease significantly when compressed, and its band gap will increase significantly when stretched. We also calculate the band gap of other strain values, and the band gap of APNR increases monotonically as the strain increases. This shows that the electronic property of APNR can be adjusted by strain engineering as needed.

4. Conclusion
The mechanical and electronic properties of APNR are studied using the first-principles calculations. We obtain the armchair APNR by cutting in the direction of the BP armchair, and discussed the reasons for its structural optimization and structural changes. The stress-strain curve and Poisson's ratio of APNR are obtained by stretching, and it is found that the fracture strain is relatively large at all widths. Its Young's modulus increases as the width increases, while Poisson's ratio is hardly changed with the increased nanoribbon width. In addition, the energy band structure of APNR is calculated and find that APNR becomes an indirect band gap compared with BP, and as the width increases, the band gap of APNR gradually decreases. Finally, we find that the band gap of APNR changes with strain and monotonically increases with strain.

References
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