A theoretical study of blue phosphorene nanoribbons based on first-principles calculations

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Based on first-principles calculations, we present a quantum confinement mechanism for the band gaps of blue phosphorene nanoribbons (BPNRs) as a function of their widths. The BPNRs considered have either armchair or zigzag shaped edges on both sides with hydrogen saturation. Both the two types of nanoribbons are shown to be indirect semiconductors. An enhanced energy gap of around 1 eV can be realized when the width decreases to \( \sim 10 \, \text{Å} \). The underlying physics is ascribed to the quantum confinement. More importantly, the quantum confinement parameters are obtained by fitting the calculated gaps with respect to their widths. The results show that the quantum confinement in armchair nanoribbons is stronger than that in zigzag ones. This study provides an efficient approach to tune the energy gap in BPNRs.

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I. INTRODUCTION

Since the successful synthesis [1,2] of monolayer graphite, i.e., graphene, significant efforts have been invested to understand its physical, chemical, thermal and other properties [3,4,5]. One most enticing among them is the high mobility of carrier confined within the two-dimensional (2D) surface [6]. This makes graphene a good candidate in semiconductor industry. However, it lacks a natural band gap, limiting its practical applications. The electronic band gap is an intrinsic property of semiconductors that determines their transport and governs the operation of semiconductor devices. To this end, many other 2D materials are explored theoretically and experimentally [7,8,9]. A search for an intrinsic energy gap is prerequisite to allow the efficient control of carriers by external field.

Unlike graphene, black phosphorus in its bulk phase is an intrinsic semiconductor with an energy gap of around 0.19 eV [10]. In theory, it can be isolated to single layer as the weak van der Waals interaction links the layers together. With this respect, two groups [11,12] independently reported that they stripped black phosphorus to few layers. Li et al. further predicted that the energy gap can be increased to be \( \sim 0.8 \) eV as black phosphorus decreases to one layer [13]. At the same time, a strain of 10% can also introduce a considerable energy gap of about 1 eV [14,15]. But, the uncontrollable strain is a challenge in experiment. Unfortunately, these gap values are still much smaller than the ideal value of \( \sim 2 \) eV, which is commonly used in electronic devices.

If we change the lattice structure of black phosphorus by little, the situation is dramatic. This is the case of monolayer of blue phosphorus (blue phosphorene), which is theoretically predicted through using \textit{ab initio} method [21]. It has an energy gap of 2 eV and thus has a great potential for practical applications. Thus, it is helpful to study its electronic properties thoroughly to broaden their use. Experimentally, single-layer phosphorus has been produced by exfoliating its bulk. If the monolayer is further cut into nanoribbons, an increase of band gap would be expected considering the quantum confinement effect. So far, the study of blue phosphorene nanoribbons (BPNRs) is still missing.

In this work, we show that BPNRs with hydrogen passivated armchair or zigzag shaped edges have indirect band gaps. In addition, the gap increases as the decrease of nanoribbon’s width, which originates from quantum confinement effect. By fitting the calculated gaps with respect to their widths, we extract the quantum confinement parameters. The results demonstrate that the quantum confinement effect in armchair BPNRs is more pronounced than that in zigzag BPNRs. For the case
of armchair BPNRs, the quantum confinement mainly dominates the lowest unoccupied states. In contrast, the quantum confinement only affects the highest occupied states for zigzag BPNRs.

The rest of this work is arranged as follows. In Sec. II we briefly describe the method used in this work. Results and discussion are represented in Sec. III. Finally, we conclude our work in Sec. IV.

II. METHOD

Our first-principles calculations are performed through using the SIESTA code within the framework of density functional theory (DFT) [22]. The generalized gradient approximation Perdew-Burke-Ernzerhof (PBE) exchange-correction functional [23] and the norm-conserving pseudopotentials are used. The plane wave energy cutoff is set to 210 Ry to ensure the convergence of total energy. The reciprocal space is sampled by a fine grid of $10 \times 1 \times 1$ $k$-point in the Brillouin zone. The conjugate gradient algorithm is taken to fully relax the geometry until the force on each individual atom is less than 0.02 eV/Å. The optimized double-$\zeta$ orbitals including polarization orbitals are employed to describe the valence electrons. Main results are checked using VASP code and a good agreement between them is obtained.

III. RESULTS AND DISCUSSION

As a start, it is necessary to test the equilibrium configuration of blue phosphorene, as shown in Fig. 1(a). The obtained lattice constant is 3.32 Å. The P-P bond length is 2.29 Å, which is slightly larger than the P-P covalent bond length ($\sim$2.2 Å) of black phosphorus [17]. The two inequivalent P atoms are distributed in two planes with a separation of 1.26 Å (see right panel of Fig. 1(a)). All the above lattice parameters agree well with the recent theoretical results [21]. According to the band structure as shown in Fig. 1(b), the blue phosphorene is indeed a semiconductor. The highest occupied states appear at the middle region along the K-Γ line, while the lowest unoccupied states are located between the Γ and M points. It reveals an energy gap of $\sim$2 eV. It should be noticed that our band structure has a slight difference from that reported by Zhu et al. [21]. In our case two occupied levels are nearly degenerate at the K point below the Fermi energy level. By contrast, a gap of around 0.5 eV appears in Zhu’s work [21]. At present, we can not understand such a divergence. The DOS of blue phosphorene is displayed in Fig. 1(c), which matches the band structure well. The very localized states appear at 1 eV below the Fermi level, corresponding the highest occupied states.

Upon cutting along different directions, two types of nanoribbons of armchair and zigzag are generated, as illustrated in Fig. 2. The same denotation as graphene nanoribbons [24] is taken for these BPNRs. Following previous convention, the armchair BPNRs are classified by the number of dimer lines ($N_a$) across the ribbon width. Likewise, zigzag ribbons are sorted by the number of the zigzag chains ($N_z$) across the ribbon width. We refer to a BPNR with $N_a$ dimer lines as a $N_a$-aBNNR and a BPNR with $N_z$ zigzag chains as a $N_z$-zBPNR.

It is well known that quantum confinement plays a key role when an infinite monolayer is cut into a nanoribbon. This quantum confinement has a direct effect on energy gap [22]. This is also true in our case. Figure 3 shows the calculated band structures of the aBPMRs for three widths. Our finding is very insightful. As the width increases, the highest occupied states remain unchanged. In contrast, the lowest unoccupied states move down, which is a direct manifestation of quantum confinement effect to aBPNRs. In order to understand this quantum confinement better, we plot the energy gaps as a function of widths, as shown in Fig. 4. As can be seen that the energy gap is close to 2.7 eV when the nanoribbon’s width is about 10 Å. This is a big improvement compared to its infinite monolayer. As the width further increases, the energy gap decreases to be $\sim$2 eV.

Next, we fit the theoretical gaps by $E = E_0 + \gamma w^{-1}$ with $E_0$ being the energy gap of blue phosphorene, $w$ the width of nanoribbons in unit of Å, and $\gamma$ the quantum...
confinement parameter in unit of eVÅ. \( \gamma \) represents the strength of quantum confinement and \( \gamma = 0 \) corresponds to non quantum confinement. Here we obtain \( \gamma = 3.93 \pm 0.18 \) eVÅ for aBPNRs. The corresponding fitted curve (solid line) is given in Fig. 4 indicating a good agreement between the calculated gaps and the fitted curve.

To examine the underlying physics of this quantum confinement effect related to the width of aBPNRs, we plot the local density of states (LDOS) of the lowest unoccupied states under the same energy range above the Fermi level, as shown in Fig. 5. As the width is small, these LDOS locate at the middle region of aBPNR (see Fig. 5(a)). They form crescent moons, showing a strong covalent manner. As the width increases, the LDOS shrink. In other words, the edge states without LDOS become enhanced. Interestingly, the LDOS seem to become spherical (see Fig. 5(c)). This means the covalent character become weaker.

In following, we switch our focus on zBPNRs. The band structures of zBPNRs for three widths are shown in Fig. 6. They are also indirect semiconductors where the highest occupied states are near the \( \Gamma \) point and the lowest unoccupied states are close to the X point. It is also found that the widths have an effect on the band structure. In contrast, this quantum confinement only acts on the highest occupied states near the \( \Gamma \) point. As the width increases, the highest occupied states are lifted up slightly, resulting in a decrease in energy gap. The detailed variation of gaps as a function of widths is displayed in Fig. 7. It explicitly shows that the energy gap increases up to be \( \sim 2.3 \) eV when the width of zBPNR is about 8 Å. If we use the above formula to fit these data, a good agreement is obtained (see the solid line in Fig. 7). The fitted quantum confinement parameter \( \gamma \) equals to \( 1.38 \pm 0.16 \) eVÅ, which is much smaller than that value (3.93\( \pm \)0.18 eVÅ) for aBPNRs. This implies that the quantum confinement in aBPNRs is stronger than that in zBPNRs.

The corresponding LDOS are displayed in Fig. 8. In contrast to aBPNRs, they distribute evenly on each P atoms. As the width is small, the LDOS are spherical (see Fig. 8(a)), showing a very localized feature. This makes the occupied states far away the Fermi energy level (see Fig. 8). As the width further increases, the LDOS exhibit a slight polarization (see Fig. 8(c) for more details), showing a more dispersion of electronic states. As a result, the highest occupied states will be lifted up. This is the origin of the band gap evolution with the widths of zBPNRs.
FIG. 7. The variation of energy gap as a function of width for ZBPRBs. The squares are the calculated values. The solid line is the fitted curve.

IV. CONCLUSION

In conclusion, we have shown that blue phosphorene nanoribbons with armchair or zigzag shaped edges all have energy gaps, which decrease as the width of the system increase. The role of the quantum confinement or the width is crucial for the values for the band gaps.

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