First-principles study of defects in blue phosphorene

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Abstract

Using first-principles density functional theory calculations, we investigate the energetics and electronic properties of Stone Wales and vacancy defects in blue phosphorene. Among these defects, the Stone Wales defect has the lowest formation energy of 1.49 eV. Single and double vacancy defects have much larger formation energies (2.35 \sim 2.90 eV). All the defects induce mid-gap bands that are relatively flat, which indicates the localized nature of the defect states. Our spin-polarized calculations further show that a single vacancy defect exhibits local magnetic moments (1.0 \mu_B), which can be attributed to the existence of an unpaired electron. Besides, we propose new types of defects with irregular buckling configurations. These new defects have even lower formation energies (1.01 and 1.30 eV). The present work may serve as an important guidance for designing and defect engineering of blue phosphorene-based devices.

1. Introduction

Defect formation is unavoidable in the synthesis and post-transfer processes of two-dimensional (2D) materials [1–4]. Indeed, defects have been extensively observed and studied in various 2D materials, including graphene [5–7], hexagonal boron nitride [8,9], silicene [10, 11], and black phosphorene [12–14]. More importantly, defects can substantially modify the electronic properties of 2D systems. For example, defect formation can produce considerable bandgap and magnetic moments in graphene, which is desirable for its applications in electronics and spintronics [15, 16]. In this regard, many efforts have been devoted to the property optimization of 2D materials by introducing defects [17–19]. Ion implantation and electron irradiation approaches have been widely used in various 2D systems to create defects in a controlled manner [20–22]. These techniques can generate different types of defects, such as vacancy, adatom, and substitutional impurity.

The formation energy of a single vacancy in graphene is approximately 8 eV, which is much larger than that (\sim 5 eV) of Stone-Wales defect [6]. It is noteworthy that the defects have much smaller formation energies (1.01–3.04 eV) in black phosphorene (BlackP) [23], indicating that their formation can be more frequent. Moreover, defects can dramatically change the fundamental properties of BlackP, such as band structures and magnetic moments [24, 25]. For example, its fundamental bandgap around 2 eV can vanish in the presence of a single vacancy [24]. It is also notable that defects can enhance the stability of BlackP in air and transform it into a dilute magnetic semiconductor [26–28].

Recently, another allotrope of phosphorus, blue phosphorene (BlueP), has emerged as a new 2D material [29]. BlueP is an indirect gap semiconductor with a bandgap of over 2 eV [30]. For producing BlueP layers, epitaxial growth approaches are available [31], which may enable its mass production. In contrast, to our best knowledge, epitaxial strategies are still incompatible with BlackP. In this regard, BlueP is also of technological importance. Because defect formation is inevitable in such an epitaxial growth, a deep understanding of defects in BlueP is a prerequisite for the applications of BlueP-based materials. However, studies of defects in BlueP are still lacking.

In this work, we used first-principles calculations within density functional theory (DFT) to systematically investigate the energetics and electronic properties of possible defects in BlueP. We first explore Stone Wales
vacancy defects broadly observed in other 2D materials. Among them, the Stone Wales defect has the lowest formation energy of 1.49 eV, which is much smaller than that of graphene. On the other hand, single and double vacancy defects have relatively high formation energies (2.35 ∼ 2.90 eV). These defects all induce flat bands within the fundamental band gap of BlueP. A single vacancy defect is found to exhibit local magnetic moments (1.0 μB). Finally, we propose new types of point defects with irregular buckling configurations. These central findings shed more light on defect formation in BlueP.

2. Computational methods

First-principles DFT calculations were performed using the projector-augmented wave method [32] and the Perdew–Burke–Ernzerhof (PBE) [33] exchange-correlation functional as implemented in the Vienna *ab initio* Simulation Package [34]. The optimized lattice constant for BlueP is 3.28 Å. Perfect BlueP was simulated by a (7 × 7) unit cell containing 98 P atoms. In all the calculations, a vacuum space of ∼20 Å was included to avoid the spurious interactions between periodic slabs. The electron densities were self-consistently converged to an energy difference of at least 10^{-5} eV. All the atoms were allowed to fully relax until the forces exerted on each atom are less than 0.01 eV/Å during structural optimization. A plane-wave basis set was employed with a kinetic energy cutoff of 400 eV, and the 2D Brillouin zone is sampled using a 2 × 2 × 1 mesh. The defect formation energy (E_{form}) is defined as E_{form} = E_{def} − N_p × E_p, where E_{def} represents the total energy of defective BlueP in question, N_p is the number of phosphorus atoms in the system, and E_p is the energy of a phosphorous atom in perfect BlueP.

![Figure 1. Optimized atomic structures of Stone Wales and vacancy defects in BlueP. Atoms with different heights are drawn in blue and sky blue colors to describe the buckled structures. The numbers represent the calculated defect formation energy.](image-url)
3. Results and discussion

We first optimized the atomic structures of the defects in BlueP. In figure 1, the optimized structures of the Stone-Wales defect and a single vacancy (SV-(5|9)) and double vacancies (DV-(5|8|5), DV-(555|777), DV-(5555|6|7777)) are displayed. Here, SV-(5|9) represents a single vacancy with 5-membered-ring and 9-membered-ring configurations around the defect. Perfect BlueP has a honeycomb-like structure similar to that of graphene, except the buckling: the calculated buckling height and the length of the P-P bond is 1.24 Å and 2.26 Å, respectively. The Stone Wales defect involves a rotation of a P-P bond around the bond center, forming two 5-membered-rings and two 7-membered-rings. The length of the rotated P-P bond decreases to 2.19 Å. Here, we consider two possible configurations for single vacancy defects, SV-(5|9) and SV-(55|66). However, only SV-(5|9) was optimized in our calculations, with a modest structural distortion near the defect. On the other hand, there are three different configurations for stable double vacancy defects, DV-(5|8|5), DV-(555|777), and DV-(5555|6|7777) structures. These single and double vacancies create new P-P bonds, which results in N-membered-ring structures, as indicated by yellow lines in figure 1.

We next investigated the formation energies of the defects in BlueP, as summarized in table 1. The cohesive energy of perfect BlueP is 3.48 eV/atom, which is almost the same as that of BlackP [23]. The Stone Wales defect
has the lowest formation energy of 1.49 eV, which indicates that the least energy is required to create the defect. This implies that the Stone Wales defect is the most probable defect among the considered defects. This energy is also much smaller than that (∼5 eV) in graphene [6], indicating that the Stone Wales defect can be more easily formed in BlueP. The other single and double vacancy defects have relatively high formation energies of 2.35 ∼ 2.90 eV. Overall, the calculated formation energies (1.49 ∼ 2.90 eV) are in the order of $E_{\text{form}}(\text{Stone Wales}) < E_{\text{form}}(\text{SV-(5|9)}) < E_{\text{form}}(\text{DV-(555|7777)}) < E_{\text{form}}(\text{DV-(5|8|5)}) < E_{\text{form}}(\text{DV-(5555|6|7777)})$. The relatively high formation energies of the double vacancies are understandable because their formation requires cleavage of more P-P bonds.

To explore the electronic modification by defect formation, we compared the band structures of the perfect and defective BlueP. Our band structure calculation shows that the perfect BlueP is an indirect-gap semiconductor with a bandgap of 1.94 eV, which agrees well with that (∼2 eV) reported in a previous DFT study [30]. As shown in figure 2, the defects create mid-gap states within the fundamental bandgap of BlueP. Therefore, the bandgap is substantially reduced, by 0.28 eV for the Stone Wales defect, 0.53 eV for DV-(555|7777), 0.56 eV for DV-(5555|6|7777), 0.84 eV for DV-(5|8|5), and 1.38 eV for SV-(5|9). In particular, SV-(5|9) has local magnetic moments (1.0 $\mu_B$), and the valence

![Figure 3. Projected densities of states (PDOS) for the neighboring atoms around the defects in BlueP. The PDOSs are obtained by integrating the PDOS of individual atoms. For comparison, the PDOS of perfect BlueP is also displayed.](image-url)
The band maximum and conduction band minimum have the opposite spin orientations. It is notable that all the mid-gap bands are flat (or nearly flat) and located below the Fermi level, which indicates that the defect states are localized.

To further explore the characters of the defect states, we plot the orbital projected densities of states (PDOS) for neighboring atoms around the defects, as shown in figure 3. For comparison, the PDOS of perfect BlueP is also shown. The perfect BlueP possesses the conduction bands that consist of the 3s and 3p orbitals and the valence bands that originate mainly from the 3pz orbital. Similarly, all the defects except SV-(5|9) show a 3pz-dominating density of states below the Fermi level. SV-(5|9) exhibits sharp peaks consisting of the 3px, and 3pz orbitals, which is corresponding to the mid-gap flat bands in the band structure. Overall, the peak positions agree well with the mid-gap bands, which indicates that the mid-gap states are localized near the defects.

It is noteworthy that SV-(5|9) in BlackP also exhibits the magnetic ground state, and the defect states consist of the 3s and 3p orbitals [23]. As shown in figure 4, SV-(5|9) in BlueP shows considerable spin densities around the defect, indicating that it gives rise to the magnetic moments owing to the existence of dangling bonds. Furthermore, we examined the interactions between two different SV-(5|9) defects in BlueP. The spins of the two SV-(5|9) are found to align ferromagnetically. Overall, such a well-localized magnetic SV-(5|9), with a small bandgap, may offer a practical route for BlueP-based spintronics.

To help distinguish the defects in future experiments, we simulate the scanning tunneling microscopy (STM) images of the defective BlueP, as shown in figure 5. The bright spots in the empty-state (+2.0 V) and filled-state (−2.0 V) STM images are mostly consistent with local atomic structures and charge distributions

Figure 4. Spin density distribution for SV-(5|9). The yellow and blue colors represent the majority (positive) and the minority (negative) densities, respectively. The spin densities are drawn with an isosurface of 0.001 (−0.001) e/bohr2.

Figure 5. Simulated filled-state (−2.0 V) and empty-state (+2.0 V) STM images of defective phosphorene: (a) SW, (b) SV-(5|9), (c) DV-(5|8|5), (d) DV-(555|777), and (e) DV-(5555|6|7777).
near the defects. For example, the empty state image of SV-(5|9) shows brighter spots around the three higher atoms near the defect, denoted in figure 5(b). Other empty-state images also exhibit similar trends that have brighter spots around higher atoms.

Besides the above frequently observed defects, we considered a new type of point defects with disorderedly buckled structures in BlueP. BlueP has a buckled honeycomb structure, within which defects with irregular buckling configurations can exist. Here we explored several buckled structures and found two different defects with low formation energy, denoted as A and B (figure 6). The formation energies are 1.01 eV and 1.30 eV for A and B defects, respectively, which are even lower than that of the Stone Wales defect. The newly proposed defects also produce flat bands within the fundamental band gap of BlueP, and, as a result, the bandgap is reduced by 0.4 eV for both configurations. Our charge character analysis further reveals that these flat bands also originate mainly from 3pz orbitals (figure 7).

Before closing, we compare the properties of defects in BlueP with those in BlackP. As shown in table 1, the defect formation energies of BlueP are mostly larger than those of BlackP, implying that these typical defects are less observable in BlueP. Instead, the newly proposed defects A and B in BlueP have much lower formation energy.
energies than those of the defects in BlackP, indicating that the formation of the new defects is more likely. It is noteworthy that the defects in BlueP cause more significant changes in the bandgap than those of BlackP. In contrast, the defects in BlueP and BlackP show similar magnetic behaviors. These findings have an important implication for defect-engineering the electronic and magnetic properties of BlueP.

4. Conclusion

We have investigated the atomic geometries, formation energies, electronic structures, and magnetic properties of various defects in BlueP based on first-principles DFT calculations. We found that the formation energies of the Stone-Wales and vacancy defects are relatively low, indicating that these defects can be formed easily in BlueP. These defects induce mid-gap flat bands, which shows the localized nature of the defect states. SV-(5\text{9}) exhibits local magnetic moments. Finally, we proposed new types of buckling defects with low formation energies. The present work may serve as a valuable guidance for future defect-engineering of BlueP-based materials.

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