Electronic and transport properties of blue phosphorene in presence of point defects: A first-principles study

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A B S T R A C T

Using the density functional theory (DFT) and non-equilibrium Green’s function (NEGF) method, we present a systematic investigation of the structural, magnetic, electronic, and transport properties of pristine and defective blue phosphorene (BlueP). The single vacancy (SV), four double vacancies (DV), and two Stone-Wales (SW) defect types are studied. The BlueP with SV (5|9) defects is a semiconductor with the magnetic moment of 0.997 μB, while DV and SW defects are non-magnetic semiconductors. The SW (55|77)-2 defect has the lowest formation energy among all of other defects under investigation. The current-voltage (I-V) characteristics of the defective BlueP indicate higher current for the both zigzag and armchair directions. The electronic, magnetic, and transport properties of defective BlueP, deviate from those of their pristine counter parts. The results may help future development of nanoelectronic and spintronic devices.

1. Introduction

Recent discoveries of new two dimensional materials has generated enormous excitement in scientific community in the last few years. Owing to their novel properties including electronic, optoelectronic, thermoelectric and spintronic, these materials have been subject to extensive studies both theoretically and experimentally. Graphene, germanene, silicene, MoS2, black phosphorene, arsenene, and borophene are only a few examples of such materials [1–8]. Wider band gap of Blue phosphorene (BlueP) and its comparable stability to those of black phosphorous has motivated researchers to focus on this new material. BlueP, a single layer of blue phosphorous, was recently proposed and synthesized [9,10]. Inside every BlueP layer, each phosphorus atom bonds with three nearest neighbors by sharing all of its three valence electrons through sp3 hybridization in a buckled honeycomb structure [11,12]. Based on DFT-PBE calculations, BlueP is a semiconductor with an indirect band gap of nearly 2 eV [9]. Several theoretical studies of BlueP have been carried out in order to utilize their fascinating features in optoelectronics [13], spintronics [14], transistors [15], negative differential resistive devices [16], and lithium-ion batteries [17].

Impurities and defects are inevitably encountered during material processing and can alter electronic, optical and magnetic properties of 2D materials [18–20]. As an example for silicene, it has been shown that single vacancy (SV), double vacancy (DV) and stone-wales (SW) defects induce different allowed energy levels within the energy gap and thus have considerable influence on the electronic properties of this material [21]. An increase in vacancy concentration reduces the magnetic moments in graphene and silicene, nevertheless, the germanene remains non-magnetic [22]. Hu et al. pointed out that a variety of point defects in black phosphorene including SV, DV and SW. The SV-(5|6) and SV-(55|66) can stimulate hole doping in black phosphorene, and that the SV-(5|9) exhibits local magnetic moments in black phosphorene different from all other defects [23]. Farooq et al. demonstrated that single vacancy defects in black phosphorous monolayer plays a role, such as p-type impurity. Furthermore, I-V characteristics of such defect along zigzag direction brought up higher current than pristine counterpart [24]. Furthermore, gas adsorption behaviors of BlueP are examined by Zhou et al., who found point defects such as SV, SW, and DV did not significantly affect the adsorption properties [25]. Due to a lack of adequate systemic study of point defects in BlueP, a comprehensive investigation of various point defects in BlueP and their effects on the structural, electronic, and transport properties of BlueP appears to be necessary.

The remainder of this paper is organized as follows: In Section 2, we describe our first-principles computational methods. Sections 3 is
devoted to the discussion of geometrical structure of the device as well as magnetic and electronic properties of pristine and defective BlueP. Finally, a conclusion is provided in Section 4.

2. Computational methods

First-principles calculations are performed using the density functional theory (DFT) approach implemented in the SIESTA package [26]. The generalized gradient approximation (GGA) with Perdew–Burke–Ernzerhof (PBE) exchange-correlation functional [27], norm-conserving pseudopotential [28] and double-zeta basis plus polarization orbitals (DZP) are used. The large \( 7 \times 4 \) supercell of BlueP (112 phosphorus atoms) with rectangular unit cell is chosen to investigate the effect of point defects in BlueP. The unit cell is shown by the shaded region in Fig. 1(a). The energy cutoff is set to 180 Ry, and the calculation orbitals (DZP) are used. The large \( 7 \times 4 \) supercell of BlueP (112 phosphorus atoms) with rectangular unit cell is chosen to investigate the effect of point defects in BlueP. The unit cell is shown by the shaded region in Fig. 1(a). The energy cutoff is set to 180 Ry, and the atomic positions are fully relaxed until the residual forces are less than 0.01 eV Å\(^{-1}\). A vacuum distance of at least 15 Å is applied along the non-periodic directions to minimize the interaction of the mirror images.

For geometry optimization and electronic structure calculation, \( 3 \times 3 \times 1 \) and \( 9 \times 9 \times 1 \) Monkhorst–Pack k-grid scheme is used to sample the Brillouin zone, respectively [29].

To check on the accuracy of the value for the lattice constant, we investigated the effect of the energy cut-off as well as the number of k-point on supercell. An increase in energy cut-off from 150 to 250 Ry, leads to a slight change in lattice parameter by 0.001 Å. In addition, increasing number of k-points from \( 3 \times 3 \times 1 \) to \( 15 \times 15 \times 1 \) causes a change of 0.00002 Å in lattice parameter.

The transport properties of BlueP are studied by non-equilibrium Green’s function (NEGF) method based on DFT as implemented in the TRANSIESTA code [30]. For transport calculations, the k-point grid is set to \( 1 \times 1 \times 110 \). The current through the contact region is obtained using the Landauer–Büttiker formula [31].

3. Results and discussions

We first investigate the geometric properties of pristine BlueP, shown in Fig. 1(a). Consistent with previous investigations [32–34], our studies predict a buckling height (h) of 1.26 Å with the P–P bond length (d) of 2.27 Å.

Subsequently, the effects of point defects on the geometrical, electronic, and magnetic properties of BlueP are explored. As depicted in Fig. 1(b), a SV (5|9) defect can be produced by removing the P\(_{29}\) atom from pristine BlueP. P\(_{28}\) and P\(_{30}\) atoms create a P–P bond in SV (5|9) defect, which saturates two of the three dangling bonds. The bond length for the new P\(_{28}\)–P\(_{30}\) is 2.52 Å, which is greater than P–P bond length of pristine BlueP. DV (5|8|5)-1 defect can be formed without dangling bonds by removing the P\(_{21}\)–P\(_{22}\) bond, see Fig. 1(c). The length of the new P\(_{20}\)–P\(_{21}\) and P\(_{14}\)–P\(_{22}\) bonds are 2.48 Å, which are larger than P–P bond length of pristine BlueP. The DV (555|777) type of the defective BlueP is created by rotating the P\(_{21}\)–P\(_{31}\) bond of DV (5|8|5)-1 type of the defective BlueP, see Fig. 1(d).

As depicted in Fig. 1(e), by rotating the P\(_{12}\)–P\(_{13}\) bond in the heptagon of the DV (555|777) defect, DV (555|5|6|777) is formed. Moreover, DV (5|8|5)-2 is created as defective BlueP, which is generated by elimination of the P\(_{21}\)–P\(_{20}\) bond, see Fig. 1(f). The bond length of the new P\(_{20}\)–P\(_{22}\) and P\(_{28}\)–P\(_{30}\) are 2.50 Å, which are larger than P–P bond length of pristine BlueP. As presented in Fig. 1(g and h), two kinds of SW defects are produced by 90° rotation of the P\(_{21}\)–P\(_{20}\) and P\(_{28}\)–P\(_{29}\) midpoints bonds, which result SW (55|77)-1 and SW (55|77)-2 defects, respectively. Consequently, the bond length of P\(_{21}\)–P\(_{20}\) and P\(_{28}\)–P\(_{29}\) is reduced from 2.27 Å to 2.21 Å for both of the SW type of the defective BlueP.

In order to evaluate the stability of point defects in BlueP, the formation energy, \( E_f \) is defined as:

\[
E_f = E_{\text{defective BlueP}} - N \times E_{\text{P}}
\]

where \( E_{\text{defective BlueP}} \) is the total energy of defective BlueP, \( N \) is the total number of P atoms in defective BlueP, and \( E_{\text{P}} \) is the energy per P atom in pristine BlueP [23]. The calculated formation energies for various point defects in BlueP are listed in Table 1. The lowest formation energy corresponds to the SW (55|77)-2 and SW (55|77)-1 defects, respectively, which is

Table 1

<table>
<thead>
<tr>
<th>Defect Type</th>
<th>( E_f ) (eV)</th>
<th>Band Gap, ( E_g ) (eV)</th>
<th>Magnetic Moment, ( M(\mu_B) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>pristine</td>
<td>0</td>
<td>1.988</td>
<td>0</td>
</tr>
<tr>
<td>SV (5</td>
<td>9)</td>
<td>2.424</td>
<td>0.516</td>
</tr>
<tr>
<td>DV (5</td>
<td>8</td>
<td>5)-1</td>
<td>2.842</td>
</tr>
<tr>
<td>DV (555</td>
<td>777)</td>
<td>2.836</td>
<td>1.467</td>
</tr>
<tr>
<td>DV (555</td>
<td>6</td>
<td>777)</td>
<td>2.933</td>
</tr>
<tr>
<td>DV (5</td>
<td>8</td>
<td>5)-2</td>
<td>2.950</td>
</tr>
<tr>
<td>SW (55</td>
<td>77)-1</td>
<td>1.470</td>
<td>1.758</td>
</tr>
<tr>
<td>SW (55</td>
<td>77)-2</td>
<td>1.404</td>
<td>1.784</td>
</tr>
</tbody>
</table>

Fig. 1. Geometric structures of (a) pristine and defective BlueP in the \( 7 \times 4 \) supercell, including the (b) SV (5|9), (c) DV (5|8|5)-1, (d) DV (555|777), (e) DV (555|5|6|777), (f) DV (5|8|5)-2, (g) SW (55|77)-1, and (h) SW (55|77)-2 defects. The unit cell is displayed by the shaded region.
about 1 eV lower than SV (5|9) defect, see Table 1. Consequently, among all the defects, the SW defects are easily produced in BlueP. This feature resembles graphene [35–37], silicon [21,38], black phosphorene [23], and arsenene [39], see Table 2. Similar to graphene and arsenene, the DV (5|8|5), DV (555|777), and DV (5555|6|7777) defects are also stable in BlueP. DV (5|8|5)-1 and DV (555|777) have around 0.1 eV lower formation energies than DV (5555|6|7777) and DV (5|8|5)-2. Accordingly, the DV (5|8|5)-1 and DV (555|777) are more stable than DV (5555|6|7777) and DV (5|8|5)-2. BlueP has a lower formation energy in comparison with graphene and silicon for the same kind of point defects [21,35–38]. Consequently, these defects are more probable for BlueP. It is important to note that all computed formation energies for BlueP are higher than those computed for arsenene [39]. This can be attributed to the larger buckling height and bond length as well as smaller cohesive energy \( E_c \) of arsenene in comparison with graphene, silicon, and BlueP [12,32–34], see Table 3. To further study the thermal stability of defective BlueP at 300 K, Ab Initio Molecular Dynamics (AIMD) simulations are performed. The canonical NVT ensemble is used, moreover the simulation time and time step are set to be 1 ps and 1.0 fs, respectively. We find that the defective BlueP are thermally stable at 300 K during the whole simulation time \( t = 1 \) ps.

The band structure of the pristine BlueP is shown in Fig. 2(a) that demonstrates a semiconducting behavior with a 1.988 eV indirect band gap. These findings are consistent with those published earlier [32,33]. The calculated band structures of the defective BlueP are illustrated in Fig. 2(b through h). As outlined in Table 1 although the different defective BlueP exhibit semiconducting behavior, their band gaps are altered by the defect type. As shown in Fig. 2(b), the band gap of SV (5|9) is reduced to 0.516 eV due to the splitting of the spin-up and spin-down bands. For DV (5|8|5)-1, DV (555|777), DV (5555|6|7777), and DV (5|8|5)-2 type defects, states are introduced in the gap, which effectively cause a reduction of the band gap to 1.305 eV, 1.467 eV, 1.507 eV, and 1.146 eV, respectively. As shown in Fig. 2(g) and (h), both SW (55|777)-1 and SW (55|777)-2 are semiconductors with the band gaps of 1.758 and 1.784 eV, respectively.

In order to investigate the impact of the point defects on the pristine BlueP electronic properties, the total density of states (TDOS) and projected density of states (PDOS) are calculated and the results are projected in Fig. 3. According to the previous studies, we also find that the valence-band maximum (VBM) of pristine BlueP mainly is originated from \( p \)-orbitals, and its conduction-band minimum (CBM) is composed of \( s \)-, \( p \)-, and \( d \)-orbitals [32,33]. As shown in Fig. 3(b), the TDOS of SV (5|9) defect reveals two defect states in the band gap, which belong to different spins, inducing a magnetic moment of 0.997 \( \mu_B \) (Table 1). In order to find the nature of the magnetism in SV (5|9) defect, the spin-polarized charge density \( \rho_{\text{spin-up}} - \rho_{\text{spin-down}} \) is also calculated. The magnetic moment in this system arises mainly from the dangling bond in P\_21 atom, see Fig. 3(b). Thus, similar to black phosphorene [23] and the arsenene [39], the SV (5|9) defect in BlueP may find potential applications in spintronic nanodevices [44]. The PDOS of SV (5|9) defect exhibits that these states originate from \( p \)-orbitals, whereas the current passing the defective BlueP increases to 0.155 (0.394) (for SW1), 0.193 (0.612) (for SW2), 0.276 (0.256) (for DV (555|777)), 0.398 (0.524) (for DV1), 0.770 (0.384) (for DV2), 0.934 (0.922) (for DV (5555|6|7777)), and 3.080 \( \mu_A \) (2.155 \( \mu_A \)) (for SV), respectively.

To gain more insight into the 1–V characteristics, the transmission spectrum along the zigzag and armchair directions at 2.6 V for the pristine and defective BlueP are calculated and the results are shown in Fig. 5. The current is entirely dependent on the transmission within the integration region based on the Landauer–Büttiker formula [24]. As illustrated, the transmission coefficient is drastically enhanced along both the zigzag and armchair directions by the SV defect, therefore implying the creation of the transport channels along the both directions. Consequently, among all the cases investigated, the SV defect has the largest current value along the zigzag and armchair directions. The inset in Fig. 5(a and b) exhibits the transmission coefficient for all systems inside the integration region along the zigzag (armchair) direction, except for the SV defect. For zigzag direction, the DV (5555|6|7777) defect indicates several peaks over an energy range of \(-1.3 \text{ eV} \)–\(-0.7 \text{ eV}\) in the transmission spectrum, however, the DV2 defect has two sharp peaks around 0.04 eV and \(-0.4 \text{ eV}\). Amongst all DV defects, the DV

<table>
<thead>
<tr>
<th>Defect</th>
<th>( E_c ) (eV)</th>
<th>BlueP</th>
<th>Graphene</th>
<th>Silicene</th>
<th>Black Phosphorene</th>
<th>Arsenene</th>
</tr>
</thead>
<tbody>
<tr>
<td>DV (555</td>
<td>777)</td>
<td>2.842–2.950</td>
<td></td>
<td>8.08 [35], 7.92 [36], 7.508 [37]</td>
<td>3.70 [21], 3.217 [38]</td>
<td>1.91–3.04 [23]</td>
</tr>
<tr>
<td>DV (5555</td>
<td>6</td>
<td>7777)</td>
<td>2.933</td>
<td></td>
<td>7.640 [37]</td>
<td>–</td>
</tr>
</tbody>
</table>
(5555|6|7777) has the largest transmission coefficient, which results in the largest current. The amplitude of transmission spectrum along the armchair direction for the SW2 is larger than DV2, accordingly the current along the armchair direction in the presence of SW2 defect is larger than DV2.

Actually, the vacancy defects in most of the 2D materials such as

![Figure 2](image_url)

**Fig. 2.** Band structures of (a) pristine and defective BlueP, including the (b) SV (5|9), (c) DV (5|8|5)-1, (d) DV (555|777), (e) DV (5555|6|7777), (f) DV (5|8|5)-2, (g) SW (55|77)-1, and (h) SW (55|77)-2 defects. The Fermi energy is set to zero and is denoted by a black dashed line. Red dashed and black lines represent the spin-up and spin-down, respectively. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

![Figure 3](image_url)

**Fig. 3.** Total density of states (TDOS), and projected density of states (PDOS) of a selected phosphorus atom in (a) pristine and defective BlueP, including the (b) P_{21} in SV (5|9), (c) P_{14} in DV (5|8|5)-1, (d) P_{20} in DV (5|8|5)-1, (e) P_{30} in DV (5555|6|7777), (f) P_{29} in SW (55|77)-1, and (h) P_{28} in SW (55|77)-2 defects. The Fermi energy is set to zero and is indicated by a black dashed line. Red dashed lines represent the spin-down. The insets display the spin charge densities of the SV (5|9) defect. The yellow and blue isosurfaces indicate the spin-up and spin-down densities. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)
Fig. 4. I–V characteristics along the (a) zigzag and (b) armchair directions of pristine and defective BlueP. The insets display the magnified I–V curves and the two-probe systems where left and right electrode regions (gray shaded region) are in contact with the scattering region.

Fig. 5. The calculated transmission spectrum along the (a) zigzag and (b) armchair directions at 2.6 V for pristine and defective BlueP, while the Fermi energy is set to zero. The insets display the magnified transmission spectrum of all systems except for the SV defect.
graphene [46] and germanene [47], can create scattering centers, which reduce the current. However, similar to black phosphorene [24], all defective BlueP create transmission channels along both armchair and zigzag directions and increase the current as compared to pristine BlueP.

4. Conclusions

In summary, using first-principles density functional theory, we investigated the geometrical structure, formation energies, and magnetic, electronic, and transport properties of three-point defect types in BlueP. Compared to graphene and silicene, these defects are more probable to form in BlueP with lower formation energies. According to the results of this study, the SW (SS)-7 defect has the lowest formation energy. The SV-(5|9) defect can induce magnetism in BlueP with a magnetic moment of 0.997 μB. The results render the SV-(5|9) defective BlueP as applicable candidates for spintronics. In contrast, the magnetic properties of BlueP are not altered by DV and SW defects, although they all create states in the band gap. The transmission coefficient is extremely enhanced along both zigzag and armchair directions by the SV defect. Finally, the current along both zigzag and armchair directions are both dependent on the point defect configuration.

CRediT authorship contribution statement

Fatemeh Safari: Conceptualization, Methodology, Software, Writing - original draft. Morteza Fathipour: Supervision, Writing - review & editing. Investigation. Arash Yazdanpanah Goharrizi: Writing - review & editing.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.physe.2019.113938.

References

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