Superior Sensitivity and Optical Response of Blue Phosphorene and Its Doped Systems for Gas Sensing Applications

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ABSTRACT: The first-principles calculation of pristine, B-, Al-, Ga-, Sb-, and Bi-doped blue phosphorene (BlueP) with adsorbed SO₂, NO, and NO₂ gas molecules including the transport and optical properties is reported. The electronic structures of pristine and doped BlueP are investigated, and the modifications in electronic band structures and density (DOS) of states are studied. The most considerable adsorption energies of BlueP after being exposed to paramagnetic gas molecules NO and NO₂ show excellent sensitivity to the considered gas molecules, which is confirmed by the current–voltage characteristics. The pristine and doped BlueP can be encouraging alternatives for new-generation optical gas sensors due to notable alterations in the pristine and doped BlueP optical spectra.

INTRODUCTION

Gas sensors play an important role in modern society to ensure safety, health, and environmental reservation. Increasing environmental pollution from factory waste and the need to quickly identify toxic gases have boosted fundamental research in material science and physics of novel materials, which can provide sufficient sensitivity at room temperature. To detect gas molecules in stable environmental situations, at room temperature, and to attain high sensitivity and selectivity, new materials are utilized in gas sensors. Two-dimensional (2D) materials have attracted strong interest owing to their irreplaceable electronic, spintronic, and optoelectronic properties. Besides, the leading characteristics of 2D materials, such as their excellent response and sensitivity, in particular, their reasonable price and lack of complexity in manufacturing, result in comprehensive utilization in gas detection applications.

Graphene and transition-metal dichalcogenides (e.g., MoS₂, WS₂) are the most commonly investigated 2D materials and have attracted attention in recent years. However, the lack of a band gap in graphene and the low room-temperature carrier mobility in MoS₂ have limited the real-world applicability of these materials.

Phosphorene (also known as black phosphorene) is a new and emerging 2D material with myriad applications based on theoretical and experimental studies. Phosphorene has a vertically corrugated structure of phosphorus atoms in a single layer. A new allotrope of black phosphorene named blue phosphorene (BlueP), which contains a more flatly single layer of phosphorus atoms, was first reported by Zhu et al. Moreover, Zhang et al. synthesized monolayer BlueP on Au(111) using molecular beam epitaxial in 2016. Similar to black phosphorene, BlueP is a semiconductor with high carrier mobility (over 1000 cm² V⁻¹ s⁻¹), which can be higher than various common 2D semiconductors, such as MoS₂ (around 200 cm² V⁻¹ s⁻¹). BlueP has an indirect and fundamental wide band gap of about 2 eV at the Perdew–Burke–Ernzerhof (PBE) level. However, due to the breaking of bond symmetry in BlueP, Dirac points can be easily distorted by introducing dopants. As a result, the indirect band gap of BlueP can be modified to a direct band gap by doping, as further described in this paper.

Besides the aforementioned outstanding properties of the new 2D gas sensing materials, they have a high surface-to-volume ratio, obvious charge transfers from host 2D materials to gas molecules, and tunable functionality of the surface for decoration species as structural merits. The gas molecule adsorption modifies the conductivity by imposing charge donors/acceptors, which is employed as a gas sensing mechanism. It is predicted that the gas molecule adsorption can influence the electrical conductivity of BlueP, thus showing that conductivity variations can improve the gas concentration detection. On the other hand, the optical responses of BlueP in the presence of gas molecules exhibit a distinct detection method compared to alternative 2D materials such as graphene, MoS₂, MoSe₂, and WS₂. Substitutional doping can act as a powerful tool to modify the electronic, optical, and...
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The adsorption process is investigated by calculating Å, respectively. After substituting B, Al, Ga, Sb, and Bi impurities into BlueP,20,21,23,24 as a gas sensor material. Although the role of BlueP,20,21,23,24 in the optical properties of BlueP and its doped system is still lacking.

Here, we explore the conductivity and optical sensing properties of pristine, B-, Al-, Ga-, Sb-, and Bi-doped BlueP with regard to the adsorption of three gas molecules: SO2, NO, and NO2 gas molecules. The Al, B, Bi, Ga, and Sb atoms are indicated in cyan, pink, green, brown, and violet colors, respectively.

RESULTS AND DISCUSSION

First, to confirm the accuracy of our results, the structural and electronic properties of pristine BlueP are investigated. The results indicate that the optimized lattice constant, bond length, and buckling height (h) of pristine BlueP are 3.27, 2.27, and 1.26 Å, respectively. After substituting B, Al, Ga, Sb, and Bi impurities into pristine BlueP, all doped BlueP structures are entirely relaxed. The compatibility of results with literature findings is good.19,25,26 To estimate the possibility of the experimental synthesis of the doped substrates, the cohesive energy (Ecoh) is calculated.27 Cohesive energies of −0.18, −0.11, −0.09, −0.12, and −0.11 eV per atom are achieved for B-, Al-, Ga-, Sb-, and Bi-doped BlueP substrates, respectively. The obtained cohesive energies prove the stability of the considered substrates. The bond lengths of the considered gas molecules are set to 1.47, 1.17, and 1.21 Å for SO2, NO, and NO2 in simulations, respectively. For SO2, the O−S−O angle is 119.99°, while the O−N−O angle for NO2 is 133.67°.28 For each adsorption case, the gas molecule is located near the substrate, and the entire system is again completely relaxed. The top and side views of the entirely relaxed structures for the adsorbed SO2, NO, and NO2 molecules are shown in Figure 1. The corresponding adsorption energies and adsorption distances are listed in Table 1. Based on the definition of Eads, a negative value denotes that the adsorption of gas molecules on the substrate is favorable energetically.29 In addition, a smaller distance between the substrate and the gas molecule can indicate a stronger interaction (Figures 2 and 3).28

In Table 1, the adsorption energy (Eads), charge transfer (ΔQ), adsorption distance (d), and band gap (Eg) of gas molecules on pristine BlueP and its doped systems are represented.
pristine and doped BlueP are dynamically stable at 300 K during the entire simulation time ($t = 1.0$ ps).

**Pristine BlueP.** As shown in Figure 1a, after full relaxation, the sulfur, nitrogen, and oxygen atoms in the SO$_2$, NO, and NO$_2$ molecules, respectively, are sited in the buckled honeycomb structure. The adsorption distances of 2.42, 1.78, and 2.43 Å are observed for SO$_2$, NO, and NO$_2$, respectively (see Table 1). Of the three gas molecules, SO$_2$ exhibits the smallest adsorption energy ($-0.17$ eV) and charge transfer ($0.17$ e on). The adsorption of NO induces great adsorption energy ($-0.22$ eV) and the largest charge transfer ($0.21$ e on) among the three considered gas molecules, indicating that the pristine BlueP monolayer is sensitive to NO. The pristine BlueP demonstrates a high sensitivity to NO$_2$ molecules with the largest adsorption energy ($-0.48$ eV) and relatively large charge transfer ($0.19$ e on). Therefore, the pristine BlueP film may be sufficient for the detection of NO and NO$_2$ gases, but may not be ideal for SO$_2$.

The effect of gas adsorption on the electronic band structures of pristine BlueP is further studied, as shown in Figure 4. The pristine BlueP semiconductor has an indirect band gap of 1.93 eV, which is the vertical distance between the conduction band minimum (CBM) placed along the $\Gamma$–$Y$ line and the valence band maximum (VBM) located at the midpoint of the region along the $T$–$Z$ line.\(^{11,19}\) The adsorption of SO$_2$, NO, and NO$_2$ reduces the band gap of pristine BlueP to 1.67, 0.65, and 0.71 eV, respectively. As a result of the spin-splitting bands with NO and NO$_2$ adsorption, the indirect band gap of pristine BlueP is smaller when exposed to NO and NO$_2$ gas molecules than SO$_2$. As a further investigation, the total density of states (TDOS) and projected density of states (PDOS) of pristine BlueP are computed before and after the molecular adsorption. The adsorption of the SO$_2$ gas molecule brings about a new defect peak at about $-0.70$ eV in the DOS (see Figure 4b). According to the paramagnetic nature of NO and NO$_2$ gas molecules, the adsorption of these gases on pristine BlueP creates significant modifications in the DOS close to the Fermi level, and these gas adsorptions lead to a magnetic moment of 1 $\mu$B. The adsorbed NO molecule brings about a spin-up defect state at about $-0.34$ eV (see Figure 4c). However, the adsorption of NO$_2$ induces two peaks in the band gap that these spin states are dissimilar, as illustrated in Figure 4d. The results shown here agree with previous studies in an utterly convincing way.\(^{21,23}\)
The obtained adsorption distances for SO$_2$, NO, and NO$_2$ molecules adsorbed on B-doped BlueP substrates are 1.31, 0.89, and 0.99 Å, respectively. According to the calculated sum of covalent atomic radii of B$^{-}$S (1.88 Å) and B$^{-}$N (1.56 Å),$^{30}$ the formation of a chemical bond between the considered gas molecules and the B-doped BlueP substrate is expected (see Figure 1b). The calculations show that $E_{ads}$ is extremely affected by the boron dopant (Table 1). Compared

Figure 3. Plane-averaged charge density difference and the side views of the charge density difference of (a) BlueP-Ga, (b) BlueP-Sb, and (c) BlueP-Bi for the adsorbed SO$_2$, NO, and NO$_2$ gas molecules along the z-direction. The yellow and blue isosurfaces represent electron accumulation and depletion, respectively. The vertical dashed lines indicate the positions of the N, O, and S atoms in the structures.

Figure 4. Band-gap structure, total density of states (TDOS), and projected density of states (PDOS) of BlueP (a) before and after (b) SO$_2$, (c) NO, and (d) NO$_2$ adsorption. The Fermi energy indicated by a black dashed line is set to zero. Red lines present spin-down in band gap diagrams. The positive and negative values represent spin-up and spin-down states, respectively.

**B-Doped BlueP.** The obtained adsorption distances for SO$_2$, NO, and NO$_2$ molecules adsorbed on B-doped BlueP substrates are 1.31, 0.89, and 0.99 Å, respectively. According to the calculated sum of covalent atomic radii of B$^{-}$S (1.88 Å) and B$^{-}$N (1.56 Å),$^{30}$ the formation of a chemical bond between the considered gas molecules and the B-doped BlueP substrate is expected (see Figure 1b). The calculations show that $E_{ads}$ is extremely affected by the boron dopant (Table 1). Compared
with the pristine BlueP, the adsorption energies of SO2, NO, and NO2 on B-doped BlueP increase to $-0.46$, $-1.37$, and $-1.05$ eV, respectively. Noticeable charge transfers of 0.49, 0.90, and 1.07 e are achieved from the B-doped BlueP system after exposure to SO2, NO, and NO2, respectively. As displayed in Figures 5a, 6a, 7a, 8a, and 9a, the band gap of the pristine BlueP is reduced after substitutional doping. In the B-doped system, the VBM and CBM are shifted to the $\Gamma$ point, making it a direct-gap semiconductor with a band gap of near 1.43 eV. The adsorption of SO2, NO, and NO2 reduces the direct band gap of B-doped BlueP to 0.80, 0.75, and 0.11 eV, respectively. As a consequence of the spin-splitting bands, the direct band gap of

![Figure 5](image1)

Figure 5. Band gap structure, total density of states (TDOS), and projected density of states (PDOS) of B-doped BlueP (a) before and after (b) SO2, (c) NO, and (d) NO2 adsorption. The Fermi energy indicated by a black dashed line is set to zero. Red lines present spin-down in band gap diagrams. The positive and negative values represent spin-up and spin-down states, respectively.

![Figure 6](image2)

Figure 6. Band gap structure, total density of states (TDOS), and projected density of states (PDOS) of Al-doped BlueP (a) before and after (b) SO2, (c) NO, and (d) NO2 adsorption. The Fermi energy indicated by a black dashed line is set to zero. Red lines present spin-down in band gap diagrams. The positive and negative values represent spin-up and spin-down states, respectively.

![Figure 7](image3)

Figure 7. Band gap structure, total density of states (TDOS), and projected density of states (PDOS) of Ga-doped BlueP (a) before and after (b) SO2, (c) NO, and (d) NO2 adsorption. The Fermi energy indicated by a black dashed line is set to zero. Red lines present spin-down in band gap diagrams. The positive and negative values represent spin-up and spin-down states, respectively.

![Figure 8](image4)

Figure 8. Band gap structure, total density of states (TDOS), and projected density of states (PDOS) of Sb-doped BlueP (a) before and after (b) SO2, (c) NO, and (d) NO2 adsorption. The Fermi energy indicated by a black dashed line is set to zero. Red lines present spin-down in band gap diagrams. The positive and negative values represent spin-up and spin-down states, respectively.
B-doped BlueP is decreased when being exposed to NO2 gas molecules, as shown in Figure 5. The TDOS of the B-doped BlueP substrate before gas adsorption is presented in Figure 5a. The adsorption of the SO2 molecule brings about a sharp peak at around 0.53 eV in the TDOS (Figure 5b). Similar to pristine BlueP, the paramagnetic nature of NO and NO2 molecules produces a magnetic moment of 1 μB. The NO molecule induces some spin-up and spin-down states, as shown in Figure 5c. Furthermore, there are apparent changes in the DOS close to the Fermi level for the adsorbed NO2 (see Figure 5d). Therefore, chemisorption occurs and a chemical bond is formed. For SO2 gas molecule adsorption, the nearest vertical distance is small compared to the sum of covalent atomic radii (2.27 Å). However, the spatial distance remains 2.53 Å (see Figure 1d and Table 1). Therefore, as was the case with the Al-doped system, no chemical bonds are expected to form. The adsorption energies of NO and NO2 on Ga-doped BlueP structures are significantly greater than pristine BlueP due to the covalent bond formation between the Ga and N atoms. In addition, the adsorption energy of SO2 on Ga-doped BlueP increases to −0.26 eV (see Table 1). The amounts of charge transferred from the Ga-doped BlueP to SO2, NO, and NO2 are 0.49e, 0.51e, and 0.86e, respectively. As shown in Figure 7a, doping with a Ga impurity causes the transition from an indirect- to a direct-gap semiconductor with a band gap of nearly 1.60 eV, similar to that observed with Al doping, with the VBM and CBM once again at the Γ point. The adsorption of SO2, NO, and NO2 reduces the band gaps of Ga-doped BlueP to 0.86, 0.64, and 1.49 eV, respectively (see Figure 7b–d). The direct-band-gap characteristic of this substrate remains unchanged after SO2 and NO2 adsorption, while the Ga-doped BlueP exhibits a direct to indirect-band-gap transition by NO adsorbent. The TDOS of the Ga-doped BlueP substrate before gas adsorption is shown in Figure 7a. The SO2 adsorption leads to some defect states within the bounds of 0.43–0.55 eV above the Fermi level (see Figure 7b). However, the paramagnetic nature of NO and NO2 gas molecules leads to a magnetic moment of 1 and 0.22 μB, respectively. As shown in Figure 7c, the NO molecule adsorption induces some spin-up and spin-down states in the gap. Furthermore, the adsorption of the NO2 molecule brings about unoccupied local states in the valence band and results in p-type semiconducting behavior by moving the Fermi level into the original valence bands (Figure 7d).

**Sb-Doped BlueP.** The sulfur atom of SO2 is fixed at the middle of the buckled honeycomb, while the NO molecule is sited at the bridge of the P–P bond after complete relaxation. The nitrogen atom of NO2 is situated in the buckled honeycomb (see Figure 1e). Adsorption distances of 2.54, 1.09, and 2.09 Å are obtained for the SO2, NO, and NO2 gas molecules adsorbed on Sb-doped BlueP substrate, respectively (see Table 1). The nearest distance for the SO2 gas molecule is greater than the covalent atomic radii of Sb–S (2.43 Å). Moreover, although the vertical distances for the NO and NO2 molecules have a smaller value than the equivalent sum of covalent atomic radii, the spatial distances are 2.12 and 2.55 Å, respectively, as given in Figure 1d and Table 1. Therefore, this system should result in no chemical bond formation. As shown in Table 1, the adsorption energies of the Sb-doped BlueP system are little compared to pristine BlueP. The amount of charge transfer for NO is 0.28e, which is larger...
than those for NO2 and SO2. As shown in Figure 8a, doping with a Sb impurity results in a transition from an indirect- to a direct-gap semiconductor with a band gap of nearly 1.73 eV at the Γ point. The adsorption of SO2, NO, and NO2 reduces the band gap of Sb-doped BlueP to 1.38, 0.41, and 0.50 eV, respectively (see Figure 8b–d). The direct-band-gap characteristic of this substrate remains unchanged after SO2 adsorption, while a direct to indirect-band-gap transition occurs by NO and NO2 adsorption. The TDOS of the Sb-doped BlueP structure before the adsorption of considered gas molecules is displayed in Figure 8a. The adsorption of SO2 leads to several defect states within the energy bounds of 0.69–0.83 eV above the Fermi level, as shown in Figure 8b. However, the paramagnetic nature of NO and NO2 gas molecules leads to a magnetic moment of 1 μB and significant modifications around the Fermi level in the DOS. The adsorbed NO gives rise to one spin-up defect state at about −0.22 eV (see Figure 8c). Furthermore, the adsorption of NO2 induces two peaks in the band gap, corresponding to different spin states, as illustrated in Figure 8d.

**Bi-Doped BlueP.** After complete relaxation, the sulfur atom from the SO2 molecule is fixed at the top of the P atom, while the nitrogen atom from the NO and NO2 molecules is sited in the buckled honeycomb (see Figure 1f). The obtained results for the SO2, NO, and NO2 gas molecules show the adsorption distances of 1.48, 1.10, and 1.80 Å, respectively (see Table 1). Although the nearest vertical distance for the studied gas molecules is smaller than their atomic radii, the spatial distances are 2.46, 2.06, and 2.90 Å, respectively, indicating that the formation of a chemical bond between the considered gas molecules and the Bi-doped BlueP substrate is unexpected. The SO2 adsorption energy on the Bi-doped BlueP is larger than the pristine BlueP. However, the adsorption energy of NO and NO2 on Bi-doped BlueP decreases to −0.21 and −0.01 eV, respectively (see Table 1). The amount of charge transfer changed for the cases of NO and NO2 adsorption to 0.38e and 0.26e, respectively, which is smaller than that of SO2. Doping with a Bi impurity results in an indirect- to a direct-gap transition with the amount of nearly 1.59 eV at the Γ point (see Figure 9a). Furthermore, the adsorption of SO2, NO, and NO2 reduces the band gap of Bi-doped BlueP to 1.52, 0.52, and 0.35 eV, respectively (see Figure 9b–d). Although the direct-band-gap characteristic of this substrate remains unchanged in the presence of SO2 adsorbent, the Bi-doped BlueP exhibits a direct- to indirect-band-gap transition through NO and NO2 adsorption. The TDOS of the Bi-doped BlueP structure before the adsorption of considered gas molecules is displayed in Figure 9a. The adsorption of SO2 brings about a slight alteration around the Fermi level, as demonstrated in Figure 9b. However, the adsorption of paramagnetic NO and NO2 gas molecules on Bi-doped BlueP leads to significant modifications in TDOS around the Fermi level. A magnetic moment of 1 μB is induced by the adsorption of these gas. The adsorbed NO causes one spin-up defect state at about −0.26 eV (see Figure 9c). The NO2 adsorption results in a spin-down impurity state at about 0.20 eV in the band gap, as illustrated in Figure 9d.

**I–V Characteristics.** The I–V characteristic along the zigzag direction is calculated based on the nonequilibrium Green’s function (NEGF) formalism to investigate the gas sensing operation of pristine BlueP and its doped structures. This measurement enables us to monitor the resistance variation in gas sensing materials. Furthermore, we can apply the I–V curve and the resistance variation as a reference to compare with experimental measurements. Owing to the structural anisotropy of BlueP, it has two transport directions, including zigzag and armchair. It should be noted that we can disregard the resistance change induced by gas molecule absorption along the armchair direction due to its low current with 1 order of magnitude compared to the zigzag direction. Therefore, this section focuses on the electrical properties of BlueP in the zigzag direction. To elucidate a better understanding of the sensing performance, the sensitivity of BlueP and its doped systems is investigated. The sensitivity is calculated using $S (%) = \frac{G - G_0}{G_0} \times 100\%$, where $G_0$ and $G$ are the conductance of BlueP and its doped structures before and after gas molecule adsorption, respectively. We estimate the value using $G = \frac{(I/I)}{(V)}$ at a potential bias of 3 V.

### Table 2. Impacts of Adsorption of Different Gas Molecules on the Conductivity of Pristine BlueP and Its Doped Systems

| Substrate | SO2 | NO | NO2 |
|-----------|-----|----|-----|
| pristine BlueP | decrease in conductivity, lowest current level at 3V | increase in conductivity (2.4–3.2) | increase in conductivity (2.4–3.2) |
| B-doped BlueP | increase in conductivity (2.4–3.2), lowest current level at 3V | increase in conductivity (2.4–3.2) | increase in conductivity |
| Al-doped BlueP | increase in conductivity, highest current level at 3V | increase in conductivity | increase |
| Ga-doped BlueP | decrease in conductivity, lowest current level at 3V | sharp increase in conductivity (2.4–2.5), highest current level at 3V | increase |
| Sb-doped BlueP | decrease in conductivity, lowest current level at 3V | sharp increase in conductivity (2.4–2.6), highest current level at 3V | increase |
| Bi-doped BlueP | increase in conductivity, lowest current level at 3V | sharp increase in conductivity (1.8–2.6), highest current level at 3V | increase |

### Table 3. Current Value, Current Ratio, and Sensitivity of Pristine BlueP and Its Doped Systems at Voltage Bias of 3 V

| Substrate | SO2 | NO | NO2 |
|-----------|-----|----|-----|
| pristine BlueP | 17.56 | 26.80 | 28.62 |
| B-doped BlueP | 27.18 | 33.22 | 38.28 |
| Al-doped BlueP | 21.90 | 17.20 | 15.65 |
| Ga-doped BlueP | 11.10 | 14.67 | 17.37 |
| Sb-doped BlueP | 9.73 | 11.95 | 19.47 |
| Bi-doped BlueP | 13.16 | 17.41 | 18.34 |
The current passing through the pristine BlueP structure is near 18.26 μA under a bias of 3 V. Nevertheless, after exposed to NO and NO2 molecules, the current of BlueP can increase sharply to 26.80 and 28.62 μA under the same bias (see Tables 2 and 3). Therefore, after adsorption of these paramagnetic gas molecules, the conductivity increases dramatically compared to pristine BlueP (see Table 3). By contrast, the current decreases to 17.56 μA when the SO2 gas molecule is adsorbed on the pristine BlueP. The sensitivity calculation of pristine BlueP also exhibits excellent sensing performance to NO2 gas molecules (see Table 3). As displayed in Figure 10b, the chemical adsorption of SO2, NO, and NO2 on B-doped BlueP brings about an enlargement of the currents passing through it compared with that of a pristine BlueP. For NO2 adsorbed, the least possible amount of voltage bias to induce noticeable current reduces from 2 to 1.2 V, which can be ascribed to spin defect states appearing at the band gap as observed in Figure 5d. Under a voltage bias of 3 V, the current passing from the B-doped BlueP region is 20.89 μA, which increases to 27.18, 33.22, and 38.28 μA when the substrate is exposed to SO2, NO, and NO2 gas molecules, respectively. When the applied bias is above 2.4 V, the current rises rapidly after the adsorption of NO gas molecule (see Tables 2 and 3). The current passing through the Al-doped BlueP sheet is smaller than pristine BlueP when exposed to NO and NO2 gas molecules. Under a voltage bias of 3 V, the current passing from the Al-doped BlueP region is 13.46 μA, which increases to 21.90, 17.20, and 15.65 μA when the substrate is exposed to SO2, NO, and NO2 gas molecules. The induced change in current after gas molecule adsorption provides enough sensitivity to suggest excellent sensing performance, as summarized in Table 3. As shown in Figure 10c, upon SO2 adsorption, the current along the zigzag direction is higher than other gas molecules under the bias of 3 V. Although B- and Al-doped BlueP structures have similar absorption energy for NO2 gas molecules, this does not essentially lead to the same electrical conductivity response. Various parameters are effective in the electrical conductivity of the films, including charge transfer, band gap value, the states around the Fermi level, and asymmetry, which is induced by each impurity in the BlueP structure. In the case of the adsorbed NO2 gas molecule on the Al-doped BlueP structure, as the calculations show, the adsorption distance is larger than that of the B-doped BlueP structure and the amount of the charge transfer and the magnetic moment are thereby also reduced. In addition, the band gap value does not change much compared to before gas absorption, and even the direct band gap is maintained. The DOS calculation also shows that, compared with the B-doped BlueP structure, the spin-down around the Fermi level is removed, which can reduce the current. In Figure 10d, we show the I−V curves of Ga-doped BlueP systems before and after gas molecule adsorption. The current 12.61 μA passes through the Ga-doped BlueP at the bias of 3 V, which is much lower than what is observed in pristine BlueP. The conductivity increases along the zigzag direction after NO and NO2 adsorption, while it is reduced after SO2 adsorption, as summarized in Tables 2 and 3. The reduction in current under SO2 adsorption shows the increase in resistance of Ga-doped BlueP, which can be a direct measure of the sensitivity in the experiment. The conductivity along the zigzag direction increases dramatically when the NO2 is adsorbed onto the Sb-doped BlueP. Although Sb-doped BlueP
structures have a small absorption energy for NO2 gas molecules, this does not essentially lead to the low electrical conductivity response. As mentioned above, several parameters are influential in determining the electrical conductivity, including charge transfer, band gap value, the states around the Fermi level, and asymmetry, which is induced by each impurity in the BlueP structure. In the case of the adsorbed NO2 gas molecule on the Sb-doped BlueP structure, as the results show, the amount of the charge transfer is large, and the magnetic moment is similar to pristine BlueP. In addition, the band gap value significantly changes compared to before gas absorption, and the DOS calculation also shows two peaks in the band gap, corresponding to different spins, as illustrated in Figure 8d. The rapid growth of current after the NO2 adsorption can be ascribed to the appearance of spin states within the band gap. The current increases from 10.31 to 19.47 μA under the bias of 3 V (see Figure 10e). At the bias range of 2.4−2.6 V, a negative resistance behavior along the zigzag direction of Sb-doped BlueP is observed after exposure to NO gas molecule. It is observed that the current of the Sb-doped BlueP system reduces to 9.73 μA when exposed to the SO2 gas molecule (see Tables 2 and 3). The current of the Bi-doped BlueP system is 11.45 μA at the voltage bias of 3 V, and it increases to 13.16, 17.41, and 18.34 μA when the substrate is exposed to SO2, NO, and NO2 gas molecules, respectively. At the voltage bias greater than 1.8 V, the current increases rapidly after the NO gas adsorption (see Figure 10f and Table 2). As summarized in Table 3, the Bi-doped BlueP exhibits high sensitivity to NO2 gas molecules.

**Optical Gas Sensing Properties.** The optical gas sensors typically provide higher sensitivity and fast response in the real-time measurement, in contrast to the conductivity-based gas detectors.31,32 Optical gas sensing properties can be evaluated from the frequency-dependent dielectric function which can be defined as \( \epsilon(\omega) = \epsilon_1(\omega) + i\epsilon_2(\omega) \), where \( \epsilon_1(\omega) \) and \( \epsilon_2(\omega) \) are the real and imaginary components of \( \epsilon(\omega) \), respectively. There is a direct relationship between the imaginary part of the dielectric function (Im[\( \epsilon \)]) and the electronic band structure, which can determine the material’s absorption properties.33 To investigate the performance of BlueP and its doped structures as an optical gas sensor, the imaginary component of the dielectric function is computed by the Kramers−Kronig formula.34 The imaginary component of the dielectric function for all substrates before and after the adsorption process is indicated in Figure 11. An extra peak is observed at lower energy than the first peak for all examined BlueP systems when they are exposed to NO or NO2 molecules (see Table 4). In the pristine BlueP structure, the extra peak of NO2 appears at a higher energy (1.29 eV) with a higher intensity compared to the NO gas molecule. However, the modification of dielectric function can be ignored by SO2 exposure, as demonstrated in Figure 11a. As shown in Figure 11b, the imaginary part of the dielectric function for B-doped BlueP dramatically changes when exposed to the considered gas molecules. The presence of the NO2 gas molecule near B-doped BlueP induces an additional peak at a lower energy than NO and SO2. A new sharp peak is observed at about 1.02 eV in the imaginary part of the dielectric function for B-doped BlueP by SO2 exposure. This peak is located at lower energies compared to B-doped BlueP, which shows the sensitivity of B-doped BlueP to SO2 gas molecule in contrast to its I−V characteristics. After SO2 gas adsorption on the Al-doped BlueP system, two extra peaks are observed at lower energy than the first peak, as shown in Figure 11c. The imaginary part of the dielectric function for Al-doped BlueP dramatically changes when exposed to the considered gas molecules. The presence of the NO2 gas molecule near Al-doped BlueP induces an additional peak at a lower energy than NO and SO2. A new sharp peak is observed at about 1.02 eV in the imaginary part of the dielectric function for Al-doped BlueP by SO2 exposure. This peak is located at lower energies compared to Al-doped BlueP, which shows the sensitivity of Al-doped BlueP to SO2 gas molecule in contrast to its I−V characteristics. After SO2 gas adsorption on the Bi-doped BlueP system, two extra peaks are observed at lower energy than the first peak, as shown in Figure 11d. The imaginary part of the dielectric function for Bi-doped BlueP dramatically changes when exposed to the considered gas molecules. The presence of the NO2 gas molecule near Bi-doped BlueP induces an additional peak at a lower energy than NO and SO2. A new sharp peak is observed at about 1.02 eV in the imaginary part of the dielectric function for Bi-doped BlueP by SO2 exposure. This peak is located at lower energies compared to Bi-doped BlueP, which shows the sensitivity of Bi-doped BlueP to SO2 gas molecule in contrast to its I−V characteristics. After SO2 gas adsorption on the Ga-doped BlueP system, two extra peaks are observed at lower energy than the first peak, as shown in Figure 11e. The imaginary part of the dielectric function for Ga-doped BlueP dramatically changes when exposed to the considered gas molecules. The presence of the NO2 gas molecule near Ga-doped BlueP induces an additional peak at a lower energy than NO and SO2. A new sharp peak is observed at about 1.02 eV in the imaginary part of the dielectric function for Ga-doped BlueP by SO2 exposure. This peak is located at lower energies compared to Ga-doped BlueP, which shows the sensitivity of Ga-doped BlueP to SO2 gas molecule in contrast to its I−V characteristics. After SO2 gas adsorption on the Sb-doped BlueP system, two extra peaks are observed at lower energy than the first peak, as shown in Figure 11f. The imaginary part of the dielectric function for Sb-doped BlueP dramatically changes when exposed to the considered gas molecules. The presence of the NO2 gas molecule near Sb-doped BlueP induces an additional peak at a lower energy than NO and SO2. A new sharp peak is observed at about 1.02 eV in the imaginary part of the dielectric function for Sb-doped BlueP by SO2 exposure. This peak is located at lower energies compared to Sb-doped BlueP, which shows the sensitivity of Sb-doped BlueP to SO2 gas molecule in contrast to its I−V characteristics.

Figure 11. Imaginary part of the dielectric function versus the photon energy for (a) pristine BlueP, (b) B-doped BlueP, (c) Al-doped BlueP, (d) Ga-doped BlueP, (e) Sb-doped BlueP, and (f) Bi-doped BlueP, before and after gas adsorption.
peaks appear at 1.05 and 2.45 eV. The first peak of Al- and Ga-doped BlueP can be intensified sharply after NO2 gas molecule adsorption (see Figure 11c,d). The adsorption of SO2 and NO induces new peaks at 0.96 and 1.23 eV for the Ga-doped BlueP system, respectively; however, the intensity of the first peak shifts to a direct band gap by doping with B, Al, Ga, Sb, and Bi atoms. Transmission spectrum analysis indicates that the adsorption of SO2 induces a new peak at 0.83 eV (see Figure 11e). The presence of NO gas molecule near Sb-doped BlueP induces several additional peaks at a lower energy compared to the first peak. Furthermore, SO2 gas molecules can lead to a new distinguished peak of about 1.65 eV at lower energies, which indicates a high sensitivity of this substrate to SO2 gas molecules (Figure 11e). This detection is not observable in I–V characteristics (see Figure 10). The adsorbed NO2 induces the largest peak at 0.83 eV (see Figure 11e). As displayed in Figure 11f, for Bi-doped BlueP, an additional peak for NO appears at a higher energy (1.07 eV) with a smaller intensity than the NO2 gas molecule. In contrast, the adsorption of SO2 does not alter the optical absorption spectrum dramatically. Table 4 summarizes the changes in the absorption spectrum of BlueP and its doped structures in the presence of different gas molecules.

### CONCLUSIONS

Based on the first-principles study, the electronic, transport, and optical properties of pristine and doped BlueP before and after SO2, NO, and NO2 gas molecules adsorption were investigated. DFT calculations reveal that the indirect band gap of BlueP shifts to a direct band gap by doping with B, Al, Ga, Sb, and Bi atoms. Transmission spectrum analysis indicates that the adsorption of considered gas molecules on pristine and doped BlueP is detectable. The current passing through BlueP and its doped systems can either decrease or increase after gas molecule adsorption, and these resistivity changes can be measured directly through experiments. The results show that B-doped BlueP can increase the sensitivity to SO2, NO, and NO2 gas molecules through strong chemical bonds. Moreover, Al- and Ga-doped BlueP can improve the sensitivity to the SO2 gas molecule. On the other hand, Sb- and Bi-doped BlueP indicate an extraordinary sensitivity to NO and NO2 gas molecules. Furthermore, these structures can be applied as sensing substances in the optical gas sensor based on dielectric function calculations. The presence of SO2 in adjacent B- and Sb-doped BlueP considerably affects the dielectric functions, and a new peak emerges about 1.02 eV and 1.65 eV, respectively. These peaks indicate the high sensitivity of B- and Sb-doped BlueP to the presence of the SO2 gas molecule, while it is not detectable from conductivity and I–V characteristics. The obtained results imply that pristine and doped BlueP systems are encouraging alternatives for gas detection and should be investigated further for future gas sensing applications.

### COMPUTATIONAL METHODS

In this study, through performing first-principles calculations based on DFT as executed in the Spanish Initiative for Electronic Simulations with Thousands of Atoms (SIESTA) package, we have investigated the electronic structures and optical properties of blue phosphorene. The generalized gradient approximation (GGA) with the Perdew–Burke–Ernzerhof (PBE) exchange–correlation functional and the double $\xi$ polarization (D2P) basis set are employed. Moreover, the DFT-D2 method of Grimme is applied to account for van der Waals interactions. All calculations are performed at a mesh cutoff energy of 150 Ry. For simulation of pristine and doped BlueP systems, a $3 \times 3$ rectangular supercell including 36 atoms is employed, as depicted in Figure 1. For geometry optimization, the relaxation of all atoms in the supercell is continued until the force on each atom is less than 0.01 eV Å$^{-1}$. To simulate pristine and doped BlueP, a $3 \times 3$ rectangular supercell with 36 atoms is employed, as depicted in Figure 1. The $k$-point sampling of $1 \times 1 \times 3$ is sufficient for geometry optimization. This $k$-grid is set to $1 \times 9 \times 9$ for the electronic structure and optical calculations. Because of paramagnetic gas molecules (NO and NO2), spin polarization is regarded in the DFT calculations. The nonequilibrium Green’s function (NEGF) formalism executed in the TRAN-SIESTA program package is employed to study the transport properties. The I–V characteristics are calculated through the Landauer–Buttiker method:

$$ I(V_d) = G_0 \int_{\mu_L}^{\mu_R} T(E, V_d) dE $$

where $G_0$ is the quantum conductance and $T(E, V_d)$ is the transmission coefficient of electrons incident at energy $E$ under a bias voltage $V_d$. The difference between the two electrochemical potentials is $E_{Rs}$. For transmission spectrum analysis, the $k$-grid is adjusted to $1 \times 1 \times 100$. The adsorption energy ($E_{ads}$) is introduced to recognize the adsorption strength of the studied systems. $E_{ads}$ can be defined as:

$$ E_{ads} = E_{BlueP+gas} - E_{BlueP} - E_{gas} + BSSE $$

where $E_{BlueP+gas}$, $E_{BlueP}$, and $E_{gas}$ are the total energy of the fully relaxed system, the energy of the isolated substrate, and the energy of the isolated gas molecule, respectively. Furthermore, to remove the artificial attraction between the substrates and gas molecules, the basis set superposition error (BSSE) is employed. Doping with different impurities induces different changes to BlueP’s charge transfer. As a consequence, the Mulliken charge analysis is employed to calculate the charge transfer between substrates and gas molecules. The adsorption distance, $d$, is the distance between the vertical coordinate of the substrate and the gas molecule (see Table 1). The negative value of charge transfer shows electron transfer from the gas molecule to the substrate, while the positive value of charge transfer represents electron transfer from the substrate to the gas molecule. To have a more detailed understanding of the interactions between the considered gas molecules and substrates, we plot the planar average charge density difference along the vertical direction in Figures 2 and 3.
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Notes
The authors declare no competing financial interest.

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