Tunable electronic properties of phosphorene by substitutional doping

Weiyang Yu,1, 2 Zhili Zhu,1 Chun-Yao Niu,1 Chong Li,1 Jun-Hyung Cho,1, 3† and Yu Jia1†

1International Laboratory for Quantum Functional Materials of Henan, and School of Physics and Engineering, Zhengzhou University, Zhengzhou, 450001, China
2School of Physics and Chemistry, Henan Polytechnic University, Jiaozuo 454000, China
3Department of Physics and Research Institute for Natural Sciences, Hanyang University, 17 Haengdang-Dong,Seongdong-Ku, Seoul 133-791, Korea

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Using first-principles density functional theory calculations, we investigate the geometries, electronic structures, and thermodynamic stabilities of substitutionally doped phosphorene sheets with group III, IV, V, and VI elements. We find that the electronic properties of phosphorene are drastically modified by the number of valence electrons in dopant atoms. The dopants with even number of valence electrons enable the doped phosphorenes to have a metallic feature, while the dopants with odd number of valence electrons keep the semiconducting feature with a larger band gap than the undoped phosphorene. This even-odd behavior is attributed to the peculiar bonding characteristics of phosphorene and the strong hybridization of sp orbitals between dopants and phosphorene. The calculated formation energies of various substitutional dopants in phosphorene show that such doped systems can be thermodynamically stable.

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The discovery of graphene has opened many new areas of research related with two-dimensional (2D) atomic-layer systems such as transition metal dichalcogenides (TMDCs), silicene, germanane, and so on.1–7 All of them have been widely studied as promising materials for future electronics applications.8–11 Most recently, few-layer black phosphorus (BP) was successfully fabricated through exfoliation techniques.2 and monolayer BP (phosphorene) is, besides graphene and silicene, another stable 2D material. Because of its intriguing electronic properties, phosphorene has drawn much attention from both experimental and theoretical works.8–12 Interestingly, phosphorene has been theoretically predicted to have a direct gap or a nearly direct gap ranging from 0.8 to 2 eV depending on the layer thickness.2 It was reported that phosphorene has a high carrier mobility of \( \sim 10^3 \) cm\(^2\)/Vs and an on/off ratio of \( \sim 10^4 \) at room temperature and thus can be applied to the channel of the field effect transistor (FET) device. Recently, Shao et al.13 presented a density-functional theory calculations shown that phosphorene is a potential superconductor materials through electron-doping. These exotic electronic properties of phosphorene nanosheets can be useful for the development of future nanoelectronic devices.14–15

Doping in 2D material systems is of fundamental importance to enable a wide range of optoelectronic and electronic devices by tuning their electronic properties. For graphene, it has been well established that carrier concentration can be modulated by charge-transfer doping from adsorbed atoms, molecules, and clusters.16–20 Here, the Fermi level can be shifted above or below the Dirac point depending on \( n \) or \( p \) doping, respectively.21 Alternatively, substitutional doping with heteroatoms via chemical vapor deposition provides an effective route for simple and stable tuning of doping levels in graphene. Unlike graphene with only one electron nonbonding to the adjacent atoms, phosphorene has one lone pair of electrons and show large anisotropic with the highest conductor band and highest valance band. Phosphorene is expected to show more colorfull and exciting properties by doping. However, the doping effect in phosphorene is less studied to our knowledge although the electronic properties of pure BP monolayer or multilayer have been extensively studied.12–15 In this work, we perform systematic studies of the substitutional doping of phosphorene with different elements. Our calculations reveal that the electronic properties of phosphorene are strongly depend on the number of valence electrons of dopant atoms that the doping systems show metallic(semiconducting) properties when the dopant atoms are even(odd) number of valence electrons. The amazing metal-semiconductor oscillation is ascribe to the peculiar electronic structures of phosphorene and the strong hybridization of sp orbits between dopants and phosphorene. Moreover, the analysis of formation energy in such systems also show that such dopant monolayer film are thermally stable.

Our DFT calculations within the general gradient approximations (GGA) have been performed using Vienna \textit{ab initio} simulation package (VASP) code.22 We used the Perdew-Burke-Ernzerhof23 exchange-correlation functional for the GGA. The projector augmented wave (PAW) method24 was employed to describe the electron interaction. The present substitutionally doped phosphorene systems were modeled in a periodic slab geometry, where a \( 2 \times 2 \) supercell of the phosphorene sheet was used in \( x \) and \( y \) directions, with a vacuum spacing of \( \sim 15 \) \( \AA \) between adjacent phosphorene sheets along \( z \) direction. Here, one P atom in the \( 2 \times 2 \) supercell was substituted by a dopant atom [see Fig. 1(a) and 1(b)], leading to a doping concentration of 6.25%. The kinetic energy cutoff of the plane-wave basis set was used to be 500 eV, and the \( k \)-space integration was done with \( 4 \times 5 \times 1 \) \( k \) points in the
FIG. 1: (color online). (a) Top and (b) side views of pure phosphorene. The bond lengths ($d_1$ and $d_2$) and bond angles ($\theta_1$ and $\theta_2$) are represented for Table I.

TABLE I: Calculated bond lengths ($d_1$ and $d_2$) and bond angles ($\theta_1$ and $\theta_2$) of B, C, N, and O doped phosphorenes, together with those of pure phosphorene. For comparison, previous theoretical results for pure phosphorene are also given.

| Dopant atom | $d_1$ (Å) | $d_2$ (Å) | $\theta_1$ (°) | $\theta_2$ (°) |
|-------------|-----------|-----------|----------------|----------------|
| pure        | 2.24      | 2.26      | 96.61          | 101.62         |
| pure$^{25}$ | 2.25      | 2.26      | 96.85          | 102.31         |
| B           | 1.95      | 1.88      | 108.68         | 122.30         |
| C           | 1.81      | 1.80      | 107.22         | 120.59         |
| N           | 1.80      | 1.80      | 104.93         | 119.02         |
| O           | 2.11      | 1.75      | 110.44         | 117.06         |

2×2 surface Brillouin zone, generated by the Monkhorst-Pack scheme.$^{25}$ All the atoms were allowed to relax until all the residual force components were less than 0.01 eV/Å.

We first optimize the atomic structure of each substitutionally doped phosphorene. In Table I, we list the calculated geometric parameters such as the bond lengths [$d_1$ and $d_2$ in Fig. 1(a) and 1(b)] and bond angles [$\theta_1$ and $\theta_2$ in Fig. 1(a) and 1(b)] in B, C, N, and O doped phosphorenes, in comparison with those of pure phosphorene. These geometric parameters of pure phosphorene agree well with those obtained by a previous calculation (see Table I).$^{25}$ We find that the $d_1$ and $d_2$ ($\theta_1$ and $\theta_2$) values in B, C, N, and O doped phosphorenes are smaller (larger) than the corresponding ones of pure phosphorene, because of the much smaller atomic radii of B, C, N and O atoms compared with P atom.

The band structures of B, C, N, and O-doped phosphorenes are calculated and presented in Figs. 2 (a). It is clear that N-doped systems present direct band gap of 0.90 eV, with its valence band maximum (VBM) and the conduction band minimum (CBM) located at $\Gamma$ point, the same as pure phosphorene which has a direct band gap of 0.88 eV. For the B-doped system, it also shows direct band gap (0.90 eV), but its VBM and CBM locate at the middle of the $\Gamma$-$X$ direction in the Brillouin zone.

Both C and O-doped systems appear metallic properties, but with different conducting direction. For the C-doped system, the Fermi level crosses the highest occupied band along the $\Gamma$-$X$ direction, corresponding to $x$ direction in the real space. However, for the O-doped systems, the Fermi level crosses the highest occupied band along the $\Gamma$-$Y$ direction, corresponding to $y$ direction in the real space. It will of great useful if we can further manipulate and use these anisotropies. It can be seen that the electronic properties of the doping systems are strongly depend on the number of valence electrons of dopant atoms. Dopant atoms with odd (even) number of valence electrons lead to semiconducting (metallic) properties in the doped systems.

To explore the general trend of the above-mentioned even-odd behaviors, we further study the substitutional doping of phosphorene with other group III, IV, V, and VI elements. The calculated band gaps in various doped phosphorenes are plotted in Fig. 2 (b). It is seen that the band gap oscillates depending on even and odd numbers of valence electrons in dopant atoms. Here, group IV (Si and Ge atoms) or VI (S and Se) doped phosphorenes that have odd number of electrons per unit cell exhibit a metallic feature with a half-filled band at the Fermi level. On the other hand, group III (Al and Ga) or V (As) doped phosphorenes containing even number of electrons per unit cell have fully occupied valence bands, showing a semiconducting feature. To exclude the situation that
the metallic cases are caused by too heavy doping, phosphorene with a lower doping concentration of 2.78% and 1.56% in supercells of 3×3 and 4×4 were also calculated, respectively, and the same metal-semiconductor rule was obtained. Additionally, the C and O co-doping was calculated with different doping configurations in the 2×4 supercell. Even the C or O doping systems are metallic, the co-doping system is surprising found to be semiconductor property, revealing that it is the average valence electrons of the dopant atoms that make the doping systems metal-semiconductor oscillating. Our results are very interesting since it is different from conventional doping effect in IV and III-VI semiconducting, where n or p doping only give some localized energy levels in the band gap.

This amazing metal-semiconductor oscillating property can be ascribe to the peculiar electronic structures of phosphorene that only three electrons involved in bonding, leaving one lone pairs non-bonding electrons per P atom. In doped phosphorenes, such non-bonding lone-pair electronic states are easily hybridized with the valence-electron states of dopant atoms, leading to the formation of delocalized electronic states near the Fermi level [see Fig. 2(a)].

To illustrate above, we plot the difference charge densities between doped system and pure phosphorene in Fig. 3 (a) for B, C, N and O-doped systems, respectively. For N-doped phosphorene, three electrons of N involved in the bonding between N and neighboring P atoms, leaving one lone pair electrons on each atom, which make the N-doped system keep the same semiconducting property as pure phosphorene. While for B-doped phosphorene, the lone pairs on B atom disappear because of the only three valance electrons bonding to neighboring P atoms, keeping also semiconducting property. As for C-doped phosphorene, there is only one electron not involved in, leading to a half-filled delocalized energy band. While for O-doped phosphorene, three non-bonding electrons also give rise to half-filled state, presenting metallic properties.

We also show in Fig. 3 (b) the total and partial density of states (PDOS) of B, C, N and O-doped phosphorene, respectively. As shown in Fig. 3 (b), the calculated PDOS projected onto the 2p orbitals of each dopant atom shows similar pattern and peak positions as compared with that for P atoms, indicating a strong hybridization of p orbitals between dopants and phosphorene. This strong hybridization leads to a broadening of the partial DOS for dopants. Especially, for C (O) doped phosphorene, the 2p partial DOS peaks of the C (O) dopant and P atoms locate at the Fermi level, thereby giving rise to a metallic property. It is the the strong coupling and hybridization just at the Fermi level that make even doping systems metallic properties.

Finally, we examine the thermodynamic stability of doped phosphorene by calculating the formation energy of substitutional doping which is defined as $E_f = (E_{tot}^{X} + \mu^X) - (E_{tot}^{P} + \mu^P)$. Here, $E_{tot}^{X}$ and $E_{tot}^{P}$ denote the total energies of X-doped phosphorene and pure phosphorene, respectively; $\mu^P$ is the chemical potential of phosphorus (taken from pure phosphorene) while $\mu^X$ is the chemical potential of X dopant atom. The calculated formation energies of B, C, N, and O doped phosphorenes are plotted as a function of $\Delta\mu^X$ in Fig. 4. We find that, if we take $\mu^X$ from the energies of orthorhombic B bulk, graphite, O$_2$, and N$_2$, the formation energies of C and N (B and O) doped phosphorenes are positive (negative), indicating an energy cost (gain) for the substitutional doping. However, all the formation energies become negative (marked with squares in Fig. 4) by assuming $\mu^X$ at their respective upper limits, i.e., at their atomic energies. Thus, we can say that the substitutional B and O dopings can be easily realized in experiments, but the substitutional C and N ones need to be particularly cautious in the synthesis processes such as atomic deposition rate, temperature, and other experimental conditions.

In summary, a series of doped systems in 2D phospho-
FIG. 4: (color online). Calculated formation energies of substitutional B, C, N and O dopings in phosphorene as a function of the chemical potential difference of each dopant atom. The reference zero of $\Delta \mu^X$ represents the chemical potential obtained from orthorhombic B bulk, graphite, N$_2$ and O$_2$, respectively. The formation energies estimated from the atomic chemical potential of each dopant are marked with square.

Phosphorene have been investigated by first-principles calculations. It is found that there is a metal-semiconductor oscillations depending on the numbers of the valence electrons of the dopant atoms. This amazing metal-semiconductor oscillation is ascribe to the peculiar electronic structures of phosphorene and the strong hybridization of $sp$ orbits between dopants and phosphorene. The estimated formation energies of the substitutional B, C, N, and O doped phosphorenes provide an information for their thermodynamic stabilities, which can be realized in experiments. The present metal-semiconductor oscillations shown here not only facilitate a deep understanding of phosphorene with defect or impurity, but also provide an intriguing route to tune the response of devices based on phosphorene materials, and attract more experimentalists to develop new phosphorene-based nanoelectronic devices. The tunable electronic properties of phosphorene will certainly pave the way for the future applications in the fields of electronic and photoelectronic materials.

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