Manipulation of magnetic state in phosphorene layer by non-magnetic impurity doping

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Abstract
Using the full-potential linearized augmented plane wave method, we have explored the structural, electronic band structure, binding energy, and magnetic properties of a non-magnetic impurity (Al, Si, S, and Cl) doped phosphorene layer. The binding energy showed a tendency to decrease with increasing atomic number. Nonetheless, we still found large binding energies of 5.1 eV ∼ 8.3 eV. We observed that the electronic band structure and magnetic property were strongly dependent on the specific impurity atom. For instance, we propose that the Al doped system will show a semiconducting transport property. In all other systems, we found metallic band structures. We predict that the Al and Si impurity act as donor elements whereas the S and Cl impurities behave as acceptor elements. Interestingly, the magnetic state appeared in Si, S, and Cl doped systems while the Al impurity induced no spin polarized state. In the Si doped system, the major contribution to a magnetic moment originated from Si impurity itself, while the presence of dangling bonds at a neighboring P atom near the impurity site plays a crucial role for magnetism in S and Cl doped systems. On the other hand, interestingly, we observed a half metallic feature in the S doped layer. Overall, we have found that the magnetic state can be manipulated by even non-magnetic impurity doping in a phosphorene layer.

1. Introduction

Very recently, a new type of 2D material, phosphorene, named after its parent black phosphorus was mechanically exfoliated by the scotch tape based microcleavage method from layered bulk black phosphorus. Single layer phosphorene was also obtained by a plasma-assisted fabrication process [1, 2]. The bulk black phosphorus has a band gap of 0.31–0.35 eV and the electronic structure of phosphorene strongly depends on the film thickness, geometry and the strain effect [3–5]. For instance, a single layer of phosphorene has a direct band gap of 1 eV in a two-dimensional structure, whereas a metallic band structure is proposed in nanoribbon geometry [6]. Due to this semiconducting feature, phosphorene may be superior to graphene for device applications in many ways. Recent studies show that few layer black phosphorene based field effect transistors have high mobility and a high on/off ratio. In addition, anisotropic electrical and optical properties have been found. Owing to these physical properties, the study of phosphorene attracts a great research interest as the next-generation 2D material for various device applications [1, 7–11].

Since a phosphorene layer consists of a non-magnetic element, an ideal phosphorene layer has no magnetic state. Therefore, most studies have focused on its electrical and optical properties because of its strong anisotropic behavior and non-magnetic characteristic [12–14]. However, many previous reports on graphene sheets, carbon nanotubes, or BN layers revealed that a magnetic state could be induced by using various methods. For instance, defect or vacancy induced magnetism in a graphene layer has been reported [15–17]. The possibility of magnetism in a graphene nanoribbon and carbon nanotube, due to the edge effect, has also been suggested [18, 19]. In addition, it was found that the substitution or doping of impurity could induce a spin polarized state. Regarding the magnetism in doped graphene systems, substitutional doping of non-metal elements (e.g. B, N, S and Si) in a graphene layer resulted in the disruption of the ideal sp² hybridization of the
carbon atoms and this caused significant changes in their electronic structures [20–22]. Similarly, the magnetism induced by the N or B adatom or vacancy defect in a BN layer has also been reported [15]. These results imply that we can tune the electronic structure of a non-magnetic 2D material and create a magnetic state through external factors. Nonetheless, it is rare to find studies on the magnetic properties of a phosphorene layer. As mentioned above, an ideal phosphorene layer displays anisotropic transport and optical properties. Thus, if one can find a way to create a magnetic state in a phosphorene layer, it will have an interesting effect on the anisotropic transport and optical properties. In this regard, we will explore the fundamental magnetic properties of an impurity doped phosphorene layer. In particular, our primary objective is to investigate the influence of non-magnetic impurity doping on the magnetic properties. To this end, we will consider Al, Si, S and Cl impurity atoms and suggest that potential magnetism can be observed due substitutional impurity doping in a phosphorene monolayer.

2. Numerical method

We have considered a 4 × 3 supercell of a phosphorene layer along x and y directions. Thus, the lattice constants of a = 13.40 and b = 13.86 Å are used and 48 atoms exist in the unit cell. With this unit cell, we replaced a single phosphorus atom by a single impurity atom. This approximately corresponds to 2.08% impurity doping. The structure optimization has been performed with Vienna ab initio Simulation Package (VASP) [23, 24]. We have used generalized gradient approximation for an exchange correlation potential with a Monkhorst pack k-point mesh of (3 × 3 × 1) and energy cutoff of 500 eV [25]. A vacuum distance of 15 Å in the z direction was imposed to avoid an artificial interaction from a neighboring cell. After the structure optimization, we used the full-potential linearized augmented plane wave method as implemented in the WIEN2K package for the magnetic and electronic structure calculations [26]. A generalized gradient approximation was used to describe the exchange and correlation potentials. Spherical harmonics with \( l_{\text{max}} = 10 \) were used to expand the charge, potential and wavefunctions in the muffin-tin region. The cutoff parameter of \( R_{\text{mt}}K_{\text{max}} = 7 \) was used to expand the wavefunction in the interstitial region, where \( R_{\text{mt}} \) is the smallest atomic sphere radius in the unit cell. \( K_{\text{max}} \) is the maximum value of the reciprocal lattice vector used in the plane wave expansion. The muffin-tin radius of 2.0 atomic units (a.u.) was used for a phosphorus atom while it was 2.24 a.u for Al, 2.08 a.u for Si, 1.98 a.u for S and 2.15 a.u for a Cl atom. A Monkhorst pack k-point mesh of (5 × 5 × 1) in the irreducible part of the first Brillouin zone has been used in our calculations and the convergence for all physical quantities investigated in the present work was carefully checked.

3. Numerical results

Figures 1(a) and (b) show the schematic illustration of the top and side views of a substitutional impurity doped 4 × 3 supercell of a phosphorene monolayer. The red, blue, and green spheres represent phosphorus atoms in the upper layer, lower layer and impurity atom (Al, Si, S, Cl), respectively. Table 1 shows the calculated bond length between the impurity atom and its three neighboring phosphorus atoms, binding energies and magnetic moments for all the doped systems.

Due to the impurity doping, phosphorus atoms in the upper and lower layer close to the impurity atom were displaced from their original positions. Because of this, we observed a lattice distortion in the surrounding of impurity atom, but the detail local structure was dependent on the specific impurity atom. We can divide our systems into two categories. The first category includes Al and Si impurities. Here, the local structures did not strongly deviate from the pristine phosphorene layer as shown in table 1. The second category consists of S and Cl impurities. In this case, we found pronounced local lattice distortions. Particularly, the distance between impurity (S or Cl) and P\(_3\) becomes larger than the sum of the covalent radii of impurity and phosphorus atoms. This means that impurity and phosphorus atoms are far beyond the bonding range and no strong chemical bond formation takes place between the impurity and P\(_3\) atom. This feature may give rise to a dangling bond at P\(_3\) in this category. We also calculated the binding energy \( (E_b) \) by using the formula

\[
E_b = E_T - E_v - E_I
\]

where \( E_T \) is the total energy of the impurity doped phosphorene. \( E_v \) represents the total energy of phosphorene layer with vacancy and \( E_I \) is the energy of the isolated impurity atom. The calculated binding energy is in the range of 5.12 ~ 8.32 eV. The Al doped layer has a maximum binding energy and it has a decreasing tendency as we move from Al to Cl, with a minimum value of 5.12 eV for Cl doped phosphorene. A high value of the binding energy reveals that the substitutional impurity doping in phosphorene systems will be highly stable.

Interestingly, we found magnetic moments induced by impurity doping and table 1 shows the calculated results. The calculated magnetic moments are 0.73, 1.0, and 0.77 \( \mu_0 \) for Si, S, and Cl doped phosphorene,
whereas we found no spin polarized state in the Al doped system. Furthermore, the magnetic moment in S and Cl doped systems had a different origin compared with Si doped layer. In Si doped phosphorene, the major contribution to the magnetic moment originated from an impurity Si atom itself. However, in S and Cl doped layers, the P3 atom in the bottom layer is a major source of spin polarization, whereas the S and Cl impurity atoms are weakly spin polarized. In figure 2, we present the band structure, total density of states (DOS), and partial density of states (p-DOS) of a pristine phosphorene layer. The ideal phosphorene layer has a band gap with no spin polarization and the p-DOS reveals that the conduction band edge is mostly built from the $p_x$ orbital while the valence band edge originates from $p_z$ orbital. To find out the modification of band structures affected by the impurity doping, we present the band structures of impurity doped systems. Figures 3(a)–(d)

Table 1. Calculated bond lengths (I–P$_1$, I–P$_2$, I–P$_3$, and I–P$_4$ in Å), binding energy ($E_b$ in eV), and magnetic moment of impurity doped phosphorene (in $\mu_B$).

|          | I–P$_1$(Å) | I–P$_3$(Å) | I–P$_4$(Å) | $E_b$(eV) | $\mu_B$ |
|----------|------------|------------|------------|-----------|---------|
| Pure phosphorene | 2.234      | 2.277      | 3.560      | ...       | ...     |
| Al-doped   | 2.359      | 2.341      | 3.336      | 8.32      | 0       |
| Si-doped   | 2.285      | 2.287      | 3.345      | 8.29      | 0.73    |
| S-doped    | 2.177      | 3.034      | 3.842      | 7.14      | 1.0     |
| Cl-doped   | 2.358      | 3.664      | 4.455      | 5.12      | 0.77    |

Figure 1. Schematic illustration of an impurity doped phosphorene monolayer: (a) top view (b) side view. I represents the impurity atom (Al, Si, S, and Cl).
represent the band structures of Al, Si, S, and Cl doped layers, respectively. The red solid lines represent the majority spin bands while the blue dotted lines are for minority spin bands. One can find that impurity doping induces substantially different band structures from one another. As compared with the pristine phosphorene layer in an Al doped system, the Fermi level is shifted toward the valance band and both majority and minority spin bands are overlapped. Thus, we found no spin polarized state. In addition, the Al doped phosphorene layer shows metallic behavior because we observed a band crossing the Fermi level near the X-point. However, the band barely crosses the Fermi level and it turns out that the DOS at the Fermi level is almost negligible. Thus, we suggest that the Al doped phosphorene may behave like a semiconductor. Interestingly, the impurity state appears near the bottom of the conduction band edge, whereas no significant change is observed near the top of the valence band edge. This result may imply that the Al impurity acts as a donor element. As expected from the magnetic moment calculations, we found spin polarized band structures in Si, S, and Cl doped systems. Unlike the Al doped case, the metallic band structure is clearly achieved in Si, S, and Cl doped systems and we observe that the spin polarized bands originate from the impurity states. Furthermore, the impurity states appear near the valence band edge and this is more noticeable in the Cl doped system, while no significant change is found near the conduction band edge. This feature suggests that the Cl impurity behaves as an acceptor element. To confirm our interpretation, we also performed the Bader charge analysis [27–29]. In the Al doped system, we found a uniform charge transfer from Al to three neighboring P atoms (P1, P2, and P3). Thus, the Al impurity atom acts as a donor element. Similarly, in the Si doped case, the uniform charge transfer from Si to three neighboring P atoms is observed although the charge transfer is relatively weak as compared with the Al doping. However, in the S doped layer, the charge transfer from P3 atoms to the S is found while the charge transfer from P1 and P2 atoms to the S was relatively weak. A similar trend was found in the Cl doped system. Overall, we have observed that Al and Si impurities act as donor elements and S and Cl impurities function as acceptor elements.

We now show the calculated total DOS and p-DOS of an impurity and its neighboring P atoms in impurity doped systems. Figure 4 shows the calculated results for Al and Si doped phosphorene layers. In the Al doped system one can find an impurity state that has a very narrow bandwidth at the edge of the conduction band. In addition, both pα and pβ orbitals of the Al impurity atom strongly contribute to the impurity band. One can also see that the pα orbital of the P2 atoms contributes to the impurity band, but its contributions are relatively weak. In the Si doped system, the strongest contribution to the magnetic moment comes from the pα and pβ orbitals of the Si impurity atom. Of course, we also find spin polarization in P3 atoms and here the pβ orbital is spin polarized. However, its contribution to a magnetic moment is rather weak. Figure 5 shows the DOS of S and Cl doped systems. In S doped phosphorene, one spin band crosses the Fermi level, while the other band is completely filled. Thus, we find a half metallic state and this results in an integer magnetic moment as displayed in table 1. From the DOS, we find that the magnetic moment mainly originates from the pβ state of the nearest phosphorus atom represented by P3. In Cl doped phosphorene, the half metallic feature disappears, but

![Figure 2. (a) Calculated band structure, (b) total DOS and PDOS for pristine phosphorene.](image-url)
we still find spin polarized states. As in the S doped case, the $p_z$ orbital of the nearest phosphorus atom (P$_3$) is the major source of spin polarization of the system. As presented in table 1, the Al doped system does not display a magnetic state, whereas all other systems show spin polarized states. We can interpret this in terms of a dangling bond and Stoner criterion. In general, the Stoner criterion implies that a physical system is more stable in a spin polarized state if the Fermi level exists at a high peak DOS. For the Al doped case, a very weak DOS is available at the Fermi level. However, we found a large DOS at the Fermi level in the Si doped system and this resulted in spin polarization. In the S and Cl doped systems, a dangling bond appeared at P$_3$ due to enhanced interatomic distance as presented in table 1. Thus, the magnetic moment originated from this dangling bond of P$_3$ atom. Previous studies also show that the dangling bond induces a magnetism in a phosphorene nanoribbon [30].

4. Conclusion

In summary, we have investigated the structural, electronic band structures, binding energy, and magnetic properties of impurity doped phosphorene layers by using the full-potential linearized augmented plane wave method. We found that the impurity doping in the substitutional site induced local lattice distortion and the detailed local geometry was dependent on the impurity atom. Among the impurity atoms we considered in this report, the most significant local distortion was found in S and Cl doped layers. The binding energy decreased from 8.3 eV to 5.1 eV as we moved from Al to Cl. In Al doped phosphorene, strictly speaking, the metallic band

Figure 3. Calculated band structure of impurity doped phosphorene: (a) Al-doped system, (b) Si-doped system, (c) S-doped system, (d) Cl-doped system. The horizontal zero line represents the Fermi level.
structure was observed, but the DOS at the Fermi level was extremely weak. Thus, the Al doped phosphorene layer will behave as a semiconductor in the transport property. Apart from the Al doped phosphorene, all other systems displayed metallic band structures. Charge analysis reveals that both Al and Si impurities act as donor elements whereas S and Cl behave as acceptor elements. These features agreed well with the calculated band structures. Consequently, we believe that the Al doped layer acts as an n-doped semiconductor regarding the transport property. Interestingly, the spin polarized state appeared in the Si, S, and Cl doped systems, whereas the Al doped layer shows no sign of a magnetic state. Furthermore, we found a half-metallic state in the S doped system. In Si doped phosphorene, the magnetic moment originates mostly from the Si impurity atom, whereas the neighboring P atoms show very weak spin polarization. In contrast, the major spin polarization originated from P near the impurity site in S and Cl doped systems, while very weak polarized states were observed in S and Cl atoms. Here, the existence of a dangling bond at P was the main source of magnetism in S and Cl doped phosphorene. Overall, we have shown that impurity doping causes a substantial change in the electronic band structure and furthermore the magnetic state can be obtained by non-magnetic impurity doping. In particular, our finding may stimulate further study regarding the spin dependent transport property.

Figure 4. Spin polarized total DOS and PDOS of impurity doped phosphorene: (a) total DOS, (b) impurity Al (c) phosphorus P, (d) phosphorus P, for the Al-doped system, and (e) total DOS, (f) impurity Si, (g) phosphorus P, (h) phosphorus P, for the Si-doped system. The vertical zero line represents the Fermi level.
Figure 5. Spin polarized total DOS and PDOS of impurity doped phosphorene: (a) total DOS, (b) impurity S, (c) phosphorus P3, (d) phosphorus P4, for the S-doped system, and (e) total DOS, (f) impurity Cl, (g) phosphorus P3, (h) phosphorus P5, for the Cl-doped system. The vertical zero line represents the Fermi level.

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