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First-principle study on electronic and optical properties of (Al, P, Al-P) doped graphene

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Abstract

First-principle calculations are used to study the electronic structures, electronic and optical properties of pure, phosphorus-doped, aluminum-doped, and co-doped graphene with phosphorus and aluminum. The results show that the band gap of graphene can be effectively opened as the carbon atoms were replaced by P and Al atoms, and a large band gap of 0.45 eV could be opened when the P and Al atoms co-replaced carbon atoms. In addition, the band gap could be also reached 0.40 eV when an Al atom replaces a carbon atom. When P is doped into graphene, the band gap value is only 0.12 eV. For co-doped graphene with phosphorus and aluminum, the lost number of the electrons which are around the aluminum (2.10 e) is smaller than that of the Al-doping graphene (2.27 e). However, the phosphorus atom loses less electrons (0.43 e) than that in P-doping graphene (1.40 e). Furthermore, the optical parameters of pure graphene and several other doped graphene systems were studied, including refractive index, dielectric function and absorption coefficient. These crucial results confirm existence of P, Al and P–Al doping induced in graphene is an effective method in band gap engineering. Our research provides the theoretical foundation of using the chemical doping with heteroatoms approach to improve the electronic and optical performances of graphene, expected to benefit the practical application of graphene in tunable optoelectronic devices.

1. Introduction

Recently, graphene as the most important two-dimensional (2D) materials has attracted enormous attention owing to its excellent properties, such as high current carrying capacity [1], carrier mobility [2, 3], Klein tunneling [4], saturation velocity [5], ambipolar effect [6], unusual quantum hall effect, thermal conductivity [7, 8] and non-zero Berry’s phase [3], leading to a wider application in catalysts [9], interconnects [10, 11], transparent electrodes [12], radio frequency transistors [13] and sensors [14]. Nevertheless, the lack of electronic band gap in graphene hugely limits the widespread use of traditional optoelectronic fields. Therefore, a great deal of efforts has been paid to open the band gap of graphene to meet the requirement for practical applications [15–18]. In recent years, scientists have discovered that doping heteroatoms in graphene can open up its band gaps and dramatically change its electronic effects and optical properties. Therefore, studying the properties of graphene by adding different atoms has become a hot topic. Deng et al [19] studied graphene mixed with different concentrations of nitrogen atoms and reported enhanced catalytic activity of pure graphene and commercial carbon black XC-72 in the cathode oxygen reduction reaction of fuel cells. Yu X et al [20] pointed out that doping P and S would greatly improve the capacitive performance of ultracapacitor in graphene, and compared the performance of intrinsic graphene and doped graphene systems. Dai et al [21] studied the
adsorption of graphene doped with boron, nitrogen, aluminum and sulfur using density functional theory, and proposed that graphene doped with B and S could be a good sensor for polluting gases such as NO and NO₂. ZHAO Chao-Jun et al [22] studied chlorine doped graphene using DFA first principle and showed that adding Cl greatly enhanced the light reflection ability of graphene. Wang et al [23] discussed the doping problem of graphene, compared the advantages and disadvantages of existing synthesis methods and preferred doping characteristics, and pointed out the different properties caused by different dopants, different doping levels and configurations, and the synergistic effect of co-dopants. Rao et al [24] studied the addition of boron and nitrogen atoms into graphene, and concluded that nitrogen-doped graphene has excellent properties when applied to supercapacitors and lithium batteries. Tylianakis et al [25] studied Li doped graphene and pointed out that doped lithium columnar oxide graphene can store hydrogen, which is a nanomaterial, and physically explained the cross-sectional energy conversion and storage. Luan et al [26] studied the structure, electrons and magnetism of graphene doped with tungsten atoms, and suggested that the spacing of tungsten atoms has an important effect on magnetism. Owen C. Compton et al [27] studied graphene oxide and indicated that graphene oxide, highly reduced graphene oxide, and graphene can be used as multifunctional blocks in carbon-based materials, where carbon nanosheets can be used as sole components in paper and film, and as fillers in polymers and inorganic nanocomposites. Therefore, it can be seen that both intrinsic graphene, doped graphene systems and oxidized graphene have certain research value and application value. Although different doping of graphene have been studied, these are not sufficient for all applications, so many scientists are still searching for better ways to use graphene in more fields.

In order to get better performance of graphene, it is necessary to change its properties through different doping. At present, the doping of P, Al and P–Al in graphene has not been studied. Therefore, this study will analyse and compare the effects of doping with P, Al and P–Al on the electron density, optical properties, state density and energy band of graphene, so as to give graphene excellent properties and provide useful value for the development of science and technology in the future.

2. Computation methods and models

2.1. Computational methods

First-principle method is the basis of the DFT (density functional theory), then geometric structure, the electrical and optical properties of graphene doped with aluminum and phosphorus can be calculated by CASTEP (Cambridge Serial Total Energy Package). Then the generalized gradient approximation (GGA) proposed by PW91 (Perdew and Wang) is used as an exchange correlation functional for optimization [28–31]. The interaction between the valence electrons and ionic core is showed by using the ultrasoft pseudopotential methods. In the calculations, k-point is set as (5 × 5 × 1), maximum energy change is set as 5.0 × 10⁻⁶ eV · atom⁻¹ and the plane wave cut-off energy is set at the most stable state which is 400 eV. During the optimization calculations, the convergence tolerances and the Self-consistent field (SCF) were set as 5.0 × 10⁻⁴ Å and 2.0 × 10⁻⁶ eV · atom⁻¹, while the max force and max stress were set as 0.01 eV · Å⁻¹ and 0.02 GPa, respectively.

2.2. Computation models

The graphene model can be obtained by cutting the optimized graphite model. Graphene is a single-layer atomic structure, its lattice is usually a symmetrical hexagonal structure. Each carbon atom forms a covalent bond with the surrounding 3 carbon atoms. The model of pure graphene has been showed in figure 1(a).

3. Results and analyses

3.1. Optimized models of doped graphene systems

The optimized models of graphene which was doped with P and Al atoms are shown in figures 1(b) and (c). When the doping sites of phosphorus atoms and aluminum atoms are different, their stability is also different, so it is necessary to find the most stable doping site. The co-doping configuration included ortho position (figure 1(d)), meta position (figure 1(e)) and para position (figure 1(f)). These different kinds of doping morphology have different forming energies. The formation energy of these three models is shown in table 1. The formation energy of ortho position, meta position and para position is −9.084, −10.813 and −10.526 respectively, and meta position has the largest formation energy and ortho position is the smallest, so the ortho co-mixing model is the most stable.

From the figures 1(b)–(f), it can be seen that the models of different doping types have some changes in the graphene. First, in P-doped graphene, the bond length of the –C bond is 1.62 Å, which is similar to the C–C bond length of pure graphene (1.42 Å). The bond length of C–Al in Al doping graphene (1.73 Å) is larger than C–C in
pure graphene. But the length of C–C bond adjacent to the C–Al bond is 1.38 Å, which is smaller than the C–C bond of pure graphene. Because the radius of the aluminum atom is large, it makes the bond length of the C–Al bond longer, which in turn makes the bond next to the C–Al bond shorter. In the P–Al co-doped graphene, the variation of the bond length of C–P, C–Al, and P–Al dopings is relatively complex, as shown in table 2.

As can be seen from table 2, among the p–Al co-doped graphene, the P–Al bond has the longest bond length, which is 1.99 Å. Meanwhile, the P–Al bond leads to the shorter bond length of C–Al bond (C1–Al and C2–Al) and P–C bond (C3–P and C4–P) than the P-doped graphene and Al-doped graphene. Thus, it can be seen that the structure of Graphene doped with P, graphene doped with Al and graphene co-doped with P–Al have all changed, so their properties have also changed.

### Table 1. $E_{\text{formation}}$ of graphene co-doped with phosphorus and aluminum at different positions.

| Doping sites | $E_{\text{formation}}$ |
|--------------|------------------------|
| ortho position | $-9.084$ |
| meta position  | $-10.813$ |
| para position  | $-10.526$ |

### Table 2. The bond length of C–P, C–Al, and P–Al in the model of figure 1(d).

| Bond types | Bond lengths (Å) |
|------------|------------------|
| C1–Al      | 1.73             |
| C2–Al      | 1.73             |
| C3–P       | 1.62             |
| C4–P       | 1.62             |
| P–Al       | 1.99             |

3.2. Electronic structures

In figure 2, it can be found that both the maximum of the valence band and the minimum of the conduction band are located at the K point of the Brillouin zone. It also demonstrates that the pure graphene is a semiconductor which has a zero bandgap. The linear dispersion relation is excellent due to the junction of the conduction and the valence band. When P, Al, and P–Al are used to dope, the energy gap of graphene will be
opened. Comparing with the pure graphene, it shows that P doping reduces the electronic energy, then makes the Fermi energy across the conduction band (figure 2(b)). By contrast, Al doping rises the electronic energy and makes the Fermi energy across the valence band (figure 2(c)). In the case of the co-doped graphene with phosphorus and aluminum, it can be found that the electronic energy level of valence band is reduced to Fermi level, while the electronic energy level of conduction band is compressed to high energy level (figure 2(d)). The band gap of P-doped graphene is 0.12 eV, that of Al-doped graphene is 0.40 eV, and that of P–Al co-doped graphene is 0.45 eV. It demonstrates that the biggest band gap of them is the P–Al doping and the smallest of them is P doping.

As can be seen from figure 3, when the band range of pure graphene is −20 eV to 5 eV, the energy comes from the C 2p and C 2s orbitals. When the band is from −20 eV to −5 eV, C 2p orbital works more and C 2s works less. When the band is between −5 eV and 5 eV, C 2p orbital works most. When P doping, the density of state will decrease to low energy due to the phosphorus. Then the Fermi energy will arrive at the conduction band (figure 3(b)). It shows that the movement of the conduction band is smaller than that of the valence band. When the range is between −1.05 eV and −0.93 eV, the graphene will open an energy gap of which the value is 0.12 eV. And impurity levels of P and C atoms range from −20 eV to 5 eV. The p orbitals of C and P are near the Fermi energy level and play an important role around the Fermi energy level. The density of states of graphene increase to high energy when Al doping. And then the Fermi level is guided to the valence band (figure 3(c)). It can be seen that the band gap of Al doped graphene is more open than that of P doped graphene. The movement of conduction band is larger than the valence band which makes the energy gap of graphene is 0.4 eV which ranges from 0.41 eV to 0.81 eV. It is different from P doping, from −10 eV to 5 eV, 3s and 3p orbitals of Al atom plays an important role. The P 3p orbital is after them. Figure 3(d) shows that P 3s works in the region which is −20 eV to −10 eV, but the Al 3s orbital has very little effect in this region. For P–Al co-doped graphene, the DOS curve of the P doping and Al doping is very different. Compared with the C–P bond for P-doped graphene, the C–P bond for co-doped graphene with phosphorus and aluminum increase to high energy. At the same time, the electron densities are dropping. The most obvious one is that C 2p is near the Fermi level. However, the reduced value of the DOS curve of the C–Al bond is larger than that of C–Al bond for Al-doped graphene (figure 3(d)). These factors are the reason why the energy gap of P–Al co-doped is larger than that of Al-doped or P-doped graphene.

In the diagram, the yellow part means the number of the electron is high, blue part means low. As can be seen from the figure, the electrons of pure graphene are evenly distributed in each lattice. After P doping, the nearby electrons of carbon atom is higher than before. But there are still little electrons around phosphorus atom. It is
obvious that the electrons moved from phosphorus to carbon atom (figure 4(b)). For Al-doped graphene, it is obvious that the density of the electrons around the aluminum atom decreased very fast, but the electrons of density around carbon atom grows also fast. It demonstrated that the aluminum provides more electrons (figure 4(c)). In co-doped graphene with phosphorus and aluminum, the electron density near the Al atom decreases rapidly, which is similar to aluminum-doped graphene. However, the electron density between the P–Al bonds is higher than the electron density between the C–Al bonds. The above conclusion is proved by the Mulliken population analysis (table 3).

It is obvious that carbon atoms are connected with others due to the sp² hybrid orbitals in the 2D plane of the graphene. The effect of hybridization is to redistribute the electrons in the s and p orbitals. Through the calculation of the pure graphene, the electrons configuration is $C s^{1.05} P^{2.95}$ (table 3). From the table 2, it is obvious that in the P-doped graphene, the carbon atom acquires electrons, the phosphorus atom loses electrons. Similarly, in Al-doped graphene, the carbon acquires electrons, the aluminum atom loses electrons. The electrons which are from the Al 3s and Al 3p move to the s and p orbitals of carbon in the Al-doped graphene. In the co-doped graphene with phosphorus and aluminum, the lost number of the electrons which are around the aluminum (2.10 e) is smaller than that of the Al-doping graphene (2.27 e). However, the phosphorus atom loses less electrons (0.43 e) than that in P-doping graphene (1.40 e). In the P–Al co-doping, the carbon atoms (C1 and C2) attached to the aluminum atoms gain more electrons than the al-doped graphene. In the P-doping graphene, the C atoms bonded to P atom gain electrons. Furthermore, the carbon atoms (C3 and C4) attached to the phosphorus atoms in the P–Al doped graphene gained fewer electrons than those in the P-doped graphene. As a result, in co-doped graphene with phosphorus and aluminum, the electrons lost by phosphorus atom which are come to carbon atoms (C3 and C4) and aluminum atoms. And this is corresponded to the electron density (As shown in figure 4).

The electronegativity of phosphorus atom is 2.19, aluminum atom is 1.61 and carbon atom is 2.55. In the P-doping graphene, the electronegativity of P atom is smaller than that of C atom, and this may cause that the phosphorus atom loses electrons and carbon atom gain electrons. In the Al-doping graphene, the electronegativity of C atom is bigger than that of the Al atom, and then the carbon atom gains electrons, the aluminum loses electrons. In the co-doped graphene with phosphorus and aluminum, aluminum atom (2.10 e) has less lost electrons than Al-doping graphene because the electronegativity of P atom bonded to Al is small, and
it is why the phosphorus loses less electrons than in P-doping graphene. Therefore, the ionicity of P–Al bond is stronger than other bond. Analysing these three systems, it is obvious that the electronegativity between the Al and C is more different than that between the P and C, then the electron between the Al and C transferred more than others (As seen in table 2). It can be seen that in P-doped graphene, the ionic stability of the P–C bond is lower than that of the Al–C bond of Al-doped graphene. As a result, co-doped graphene with phosphorus and aluminum, the ionicity is higher than the other two doping, and the P–C bond has the most stable covalency.

### 3.3. Optical properties

Figure 5 shows the complex refractive index of graphene under different doping conditions. The formula for the complex refractive index \( N \) is as follows:

\[
N = n + ik
\]

The real part \( n \) represents the refractive index, and the imaginary part \( k \) represents the extinction coefficient. It can be seen from the figure 5(a) that the refractive index of pure graphene keeps the downward trend and extinction coefficient of pure graphene has three peaks between 0 eV and 5 eV. The peaks of extinction
The extinction coefficient appear approximately at 1.28 eV and 4.25 eV. For P-doped graphene, the peaks of extinction coefficient and refractive index are shifted, moving to lower energy, and the intensity is reduced. For Al-doped graphene, the extinction coefficient and the refractive index curve changes significantly, sharp peak refractive completely disappeared, shifts to soft peaks. At the same time, the high-frequency peak of the extinction coefficient becomes wider, the low-frequency peak becomes smaller. The complex refractive index and extinction coefficient of phosphorus atom doped with aluminum atom are very close to the curves of aluminum atom doped alone. But at this point co-doping causes the complex refractive index to move to lower energies, the peak of the extinction coefficient is slightly wider and the intensity is reduced.

Figure 6 shows the real and imaginary parts of the complex dielectric function of graphene under different doping conditions. It is not difficult to find that the curves of the real and imaginary parts of the complex dielectric function are akin to the curves of the refractive index (n) and extinction coefficient (k) of the complex refractive index (N), respectively. In doped graphene systems, the curves of real part and imaginary part of dielectric function are similar to refractive index and extinction coefficient. However, the difference is the range of the ordinate. It can be seen from figure 6(a) that in the low frequency range (0–2.5 eV), The dielectric function of phosphorus decreased sharply. In the range of 2.5 eV to 5 eV, the peak in the real part of the dielectric function for pure graphene is the strongest (1.56), then P-doping graphene (1.21), Al doping graphene (1.07). When the abscissa of the curve is 0 (the energy is 0 eV), the static dielectric constant is equivalent to the real part of the dielectric function. The dielectric constants of pure graphene, P-doped graphene, Al-doped graphene and P–Al doped graphene are respectively 4.81, 99, 5.29, and 9.87. It can be found that the doping of phosphorus atoms makes the dielectric function become very large. Among them, the biggest change is P doping, followed by P–Al co-doping and finally Al doping.

As can be seen from figure 6(b), the curve trend looks like the real part in the low frequency range (0 ~ 1.74 eV) and the dielectric function of phosphorus is decreasing rapidly. Meanwhile, the low frequency peak has been showed that pure graphene is 2.02, Al-doping is 2.19, P–Al co-doped is 3.26. And in the range of 2.5 eV to 7.5 eV, the value of the peak strength has been showed in figure 6(b), pure graphene (1.96), P-doped graphene (2.01), Al-doped graphene (1.49), P–Al doped graphene (1.48). For the low energy region of pure graphene, the peak value of the imaginary part corresponds to the transition of the P–P band; in the high energy region, the peak value of the imaginary part corresponds to the transition of the S–P band. The electron
transitions between C 2p and C 2p, C 2p and P 3p orbitals cause phosphory-doped graphene to peak in the low energy region. The electron transitions between C 2s and C 2p, and between C 2s and P 3p, their orbitals cause phosphorous-doped graphene to peak at high energies. The electron transitions between c2p and c2p, c2p and al3p lead to the peak of Al doped graphene in low energy region. The electron transitions between C 2s and C 2p, sp of A and C 2p , c2p and Al 3s lead to the peak of Al doped graphene in the high energy region. The electron transition between C 2p and P 3p, Al 3p and C 2p, C 2p and C 2p leads to the peak value in the low energy region. The electron transitions between the orbitals of C 2s and P 3p, Al spand C 2p, Al 3s and C 2p, C 2p and C 2p lead to the peak value of P -Al co-doped graphene in the high energy region.

The complex dielectric function \( \varepsilon = \varepsilon_1 + i\varepsilon_2 \) has the following relationship with the complex refractive index \( N \):

\[
\varepsilon = N^2
\]

Here, \( \varepsilon_1, \varepsilon_2 \) are the real part and imaginary part of the complex dielectric function, while \( n \) is the refractive index and \( k \) is extinction coefficient. Their relationship is as follows:

\[
\varepsilon_1 = n^2 - k^2
\]

\[
\varepsilon_2 = 2nk
\]

The results show that the real part of the dielectric function is inversely proportional to the extinction coefficient with the increase of the refractive index, and the imaginary part is positively proportional to the extinction coefficient with the refractive index. Because the absorption coefficient is affected by the imaginary part of the dielectric constant, we only study the change of the imaginary part. From figure 6(b), we can see that in the low frequency range, the peak intensity of the imaginary part of various graphene is sorted as: P–Al doped graphene, Al-doped graphene, pure graphene, and P-doped graphene, while high frequency range are P-doped graphene, pure graphene, Al-doped graphene and P–Al-doped graphene, the orders of the peak intensity of the refractive index and extinction coefficient of different graphene in the low and high frequency ranges are different.

Figure 7 shows the light absorption of doped graphene systems under different conditions. The relationship between light absorption coefficient and extinction coefficient is as follows:

\[
\eta = \frac{2k\omega}{c}
\]

In the publicity, \( c \) represents the speed of light and \( \omega \) represents the frequency. Visible light absorption \( \eta \) is Proportional to \( k \), which is very consistent with the extinction coefficient. And the curve is the same as the curve of the extinction coefficients. After doping it can be found that the absorption peaks become weaker, especially P–Al-doped graphene, which is also the cause of the band gap opening.

4. Conclusion

According to the first principles calculation, the electrical and optical properties of pure graphene, phosphorus doped graphene, aluminum doped graphene and graphene co-doped with phosphorus and aluminum were calculated and compared. The results show that pure graphene is a semiconductor material with the property of zero-band gap. When P, Al and P–Al impurities are added, its optical and electrical properties will change. These
different doping methods can open the zero band gap of graphene and change its properties. The band gap width of P–Al co-doped graphene is 0.45 eV, and that of Al-doped graphene and P-doped graphene are 0.40 eV and 0.12 eV, respectively. After P doping, phosphorus loses electrons, carbon gains electrons, and carbon gains electrons mostly from the 3p orbital and a little from the 3s orbital. When Al-doped graphene, aluminum will lose electrons, carbon will gain electrons. In the P–Al co-doped graphene, the number of electrons lost by aluminum atom is less than that of aluminum atom in aluminum doped graphene. At the same time, in P–Al co-doped graphene, the number of electrons lost by phosphorus atom is also less than that of phosphorus atom in phosphorus doped graphene. When phosphorus and aluminum atoms replace carbon atoms, the absorption peak of doped graphene systems is weaker than that of the intrinsic graphene, and the absorption peak of doped graphene with P–Al is very obvious. The absorption image of graphene co-doped with phosphorus and aluminum looks very similar to that of intrinsic graphene. It not only provides a theoretical basis for the application of graphene in wide band gap semiconductors, but also offers a feasible research direction for the widely used graphene-like doped systems.

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Figure 7. Optical absorption of pure and different doping types in the graphene.
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