Islamic Azad University

Journal of
Optoelectronical Nanostructures

Winter 2017 / Vol. 2, No. 1

Energy band correction due to one dimension tension in phosphorene

Ali Izadparast[*1], **Peyman Sahebsara**[1]

1 Department of Physics, Isfahan University of Technology. Isfahan, Iran

(Received 26 Dec. 2016; Revised 22 Jan. 2017; Accepted 20 Feb. 2017; Published 15 Mar. 2017)

Abstract: Among graphene-like family, phosphorene is a typical semiconducting layered material, which can also be a superconductor in low temperature. Applying pressure or tension on phosphorene lattice results in changing the hopping terms, which change the energy bands of the material. In this research we use the tight-binding Hamiltonian, including relevant hopping terms, to calculate energy bands of normal and under tension phosphorene. Our results show that the energy gap decreases by decreasing t_2/t_1 from 3 to 2, and finally the gap disappears.

Key words: phosphorene, band structure, electron conductivity, tension, energy

band gap**.**

1. INTRODUCTION

Two dimensional (2D) materials such as monolayer graphene and monolayer transition metal dichalcogenide (TMDC) MoS_2 have attracted intensive research interests owing to their interesting electronic, mechanical, optical, or thermal properties, some of them not seen in their bulk counterparts, for example, the massless Dirac-fermion behavior of the grapheme [1,2,3].

Recent success in isolation of ultrathin layers of black phosphorus has raised interest for its electronic properties [4]. Black phosphorus is also a layered structure in which the layers are held together by Van der Waals interactions [5]. Each layer consists of phosphorus atoms that are covalently bonded to three

---

[*] **Corresponding author. E-mail: izadparast.physics@gmail.com**

next to phosphorus atoms, thus forming a puckered honeycomb structure because of $sp3$ hybridization, as shown in Fig. 1. As can be seen, the phosphorus sites are grouped in two zigzag layers [6,7]. The upper and lower sites are shown with darker and lighter colors, respectively. Phosphorene can also be isolated from black phosphorus via mechanical exfoliation [8]. Inside the phosphorene layer, each P atom is bonded with three neighboring P atoms, forming a puckered honeycomb structure similar to graphene. However, unlike zero-bandgap graphene, layered phosphorus has a direct band gap of 0.3 eV in the bulk form, which can increase up to 1.0-1.5 eV for an isolated monolayer [9].

The presence of an significant direct band gap and high carrier mobility [10] make few-layer black phosphorus a promising candidate for novel semiconductor applications. From the point of view of practical applications, the influence of environment plays a crucial role in the performance of potential 2D electronic devices [11,12].

There are already several works based on first-principle calculations. The tight-binding model was proposed by including the transfer energy t_i over the 5 neighbor hopping sites (i = 1, 2, · · · , 5), as illustrated in Fig. 1. It has been shown that it is enough to take 5 hopping links, as illustrated in Fig. 1. The transfer energy explicitly reads as t_1=−1.220 eV, t_2= 3.665 eV, t_3= −0.205 eV, t_4= −0.105 eV, t_5= −0.055 eV for these links. This implies that the zigzag chains have negative $t_1$hopping integrals along the chains and positive t_2 hopping integrals connecting these chains [14].

Because of the closeness of considered orbitals, the values of t_1 and t_2 are more noticeable than other hoppings. The sign of hopping integrals from crystal potentials is determined and for example the plus sign of t_2 somehow shows the hole like behavior. Other hopping terms are negative. From these discussions it can be concluded that the first two hoppings have the most important role in the electronic band structure of phosphorene, so calculations are carried out on the basis of these two hoppings. Here t_1 is considered the constant and t_2 varies with respect to t_1. As it can be seen from the value of hoppings $t_2=3|t_1|$. Therefore by applying tension in a specific direction, for example horizontal direction, the changes of lattice constant and also the first two hopping terms are investigated.

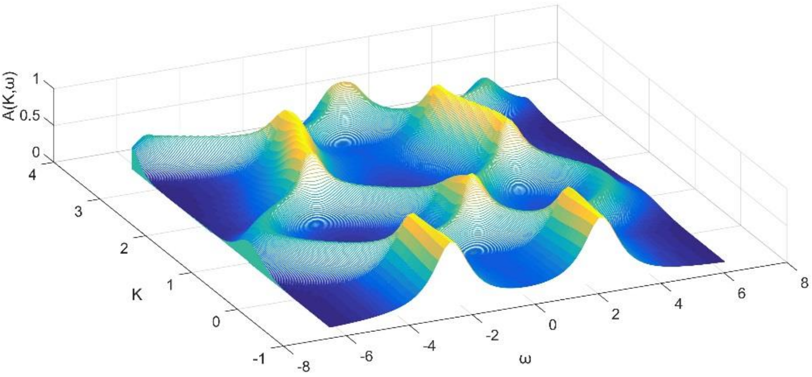

Fig. 1 (a) Crystal structure and hopping term $t_i$of single layer phosphorene for the TB model. (b) Top view. Note that the blue (red) balls represent the phosphorus atoms in the upper (lower) layer. The dotted rectangle indicates a primitive unit cell containing four atoms. The parameters for the bond angles and unit cell lengths are taken from ref. [13].

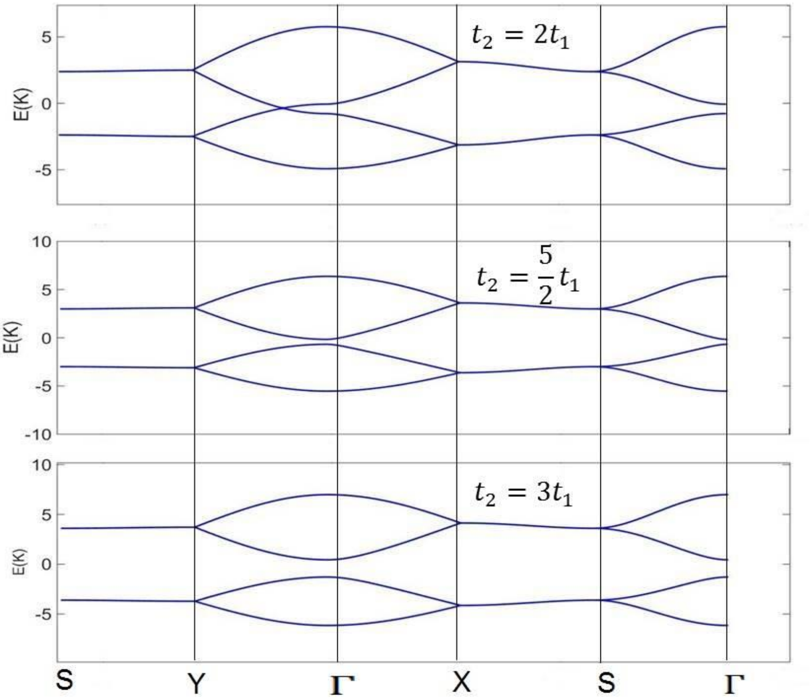

Fig. 2 The band structure of phosphorene without tension. There are two degeneracy in this figure.

In this paper, the band structure of phosphorene is studied in section 2 and in the band structure of phosphorene will be calculated in the presence tension in section 3. Section 4 deals with spectral function and density of states (DOS). Finally section 5 will be devoted to conclusion.

2. Band structure of Phosphorene

In this paper, we use the Tight Binding (TB) model to obtain band structure of a crystal. The TB Hamiltonian reads as [15]

$$H = \sum_{i,j} t_{ij} c_i^{\dagger} c_j \qquad (1)$$

Where the summation is over the lattice sites, and t_{ij} are the hopping integrals between the *i*th and *j*th sites. Further, $c_i^{\dagger}$ and c_j represent the creation and annihilation operators of electrons in sites *i* and *j*, respectively. These hopping integrals between a site and its neighbours are shown in Fig. 1(a).

The connections in the upper or lower layers in each zigzag chain are represented by t_1 hopping integrals, and the connections between a pair of upper and lower zigzag chains are represented by t_2 hopping integrals. Further, t_3 denotes the hopping integrals between the nearest sites of a pair of zigzag chains in the upper or lower layer, and t_4 denotes the hopping integrals between the next nearest neighbor sites of a pair of upper and lower zigzag chains. Finally, t_5 is the hopping integrals between two atoms on the upper and lower zigzag chains that are farthest from each other. In the momentum representation the 4-band Hamiltonian reads as

$$H = \begin{pmatrix} 0 & h_1(K) & h_2(K) & h_3(K) \\ h_1^*(K) & 0 & h_4(K) & h_2(K) \\ h_2^*(K) & h_4^*(K) & 0 & h_1(K) \\ h_3^*(K) & h_2^*(K) & h_1^*(K) & 0 \end{pmatrix} \qquad (2)$$

Whose elements are given by

$$h_1(K) = t_2 + t_5 \exp(-ik_x a)$$

$$h_2(K) = 4t_4 \exp(-i/2(k_x a - k_y b)) \cos(k_x a/2) \cos(k_y b/2)$$

$$h_3(K) = 2\exp(i\,/\,2(k_y b))\cos(k_y b\,/\,2)(t_1\exp(-i\,/\,2(k_x a)) + t_3) \qquad (3)$$

$$h_4(K) = 2\exp(i\,/\,2(k_y b))\cos(k_y b\,/\,2)(t_1 + t_3\exp(-i\,/\,2(k_x a)))\,.$$

The Above matrix is Hermitian and gives real eigenvalues which are the bands energy. By doing so, we are provided with four eigenvalues equtions, each of them is a function of vector K. As shown in figure.2, the bands are nearly symmetrical and degeneracy between the two bands in direction of X-S and S-Y can be seen. More ever, in the calculations, we obtain 1.8 eV for band gap, which as opposed to graphene, there are no Dirac point in the bands. These comments lead us to the conclution that phosphorene is a semiconductor.

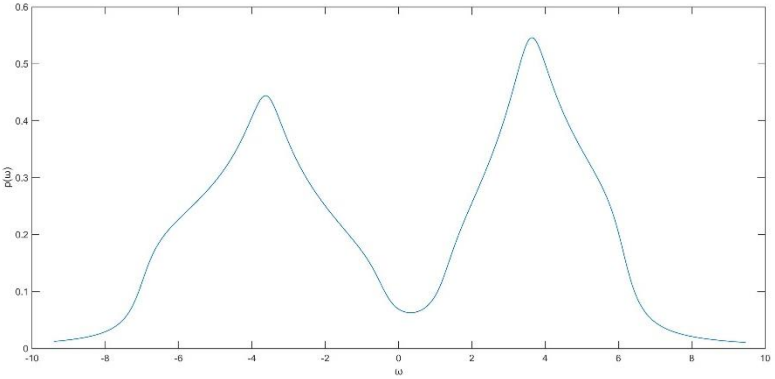

Fig. 3 Indicating the band structure when tension has applied. (a) A conductor, t_2=2|t_1|. (b) A gap has created around 0.5eV for t_2=5/2|t_1|. (c) Similar to real band structure without tension for t_2=3|t_1|.

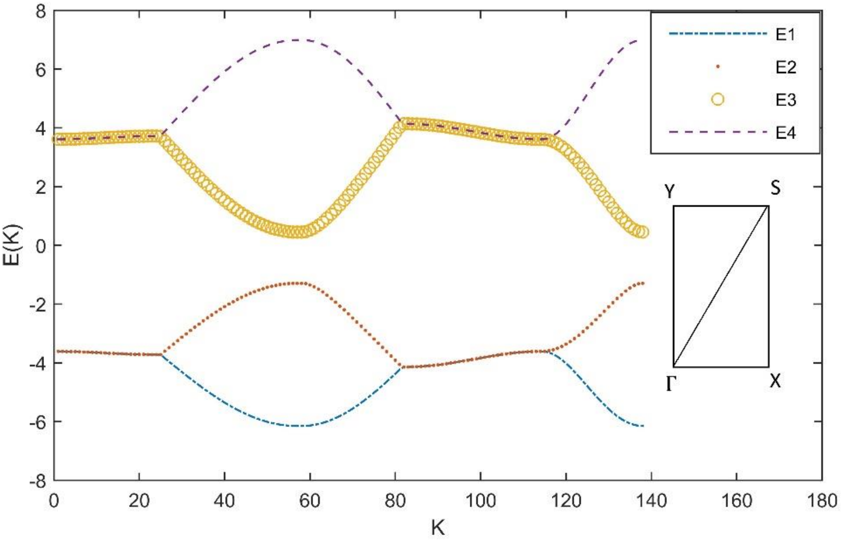

Fig. 4 : local density of states for t_2=2|t_1| and for 5 directions considered in band structures.

3. Strain in phosphorene lattice

Deformation of structure of phosphorene lattice would bring about changing in hopping. In this case the lattice constants increases and the strength of hoppings decreases. In this paper, we apply changing in hoppings, and as a result the changes in bands will be studied. we set t_1 fixed and change t_2 relative to that. The reason of choosing these two hoppings, as was mentioned, is their role, which is assumed to be more than other hoppings.

It should also be noted that tension is applied in the horizontal direction and approximately 10 to 20 percent of real value of lattice constants decreases along the horizontal direction. As shown in Fig. 3 the material changes into different phases and band structures vary a lot for three given values.

In this figure, tension effect in lattice is completely noticeable, it is because a phase change in phosphorene is observed. In Fig. 3 (a) bands show a dirac point for t_2=2|t_1|. In these conditions a phase change is observed in phosphorene which has transferred from semiconductor there to conductor. Good result can be seen in this figure because phosphorene is known as a semiconductor without a dirac point. In Fig. 3 (b) there is still gap between bands but gap size in comparison with normal condition has decreased and reached 0.5 eV. In this figure the relation between the first and the second hopping is t_2=5/2|t_1|. Finally, Fig. 3 (c) shows band structures similar to real band structure of phosphorene without tension. In this figure, gap is nearly 1 eV and t_2=3|t_1|.

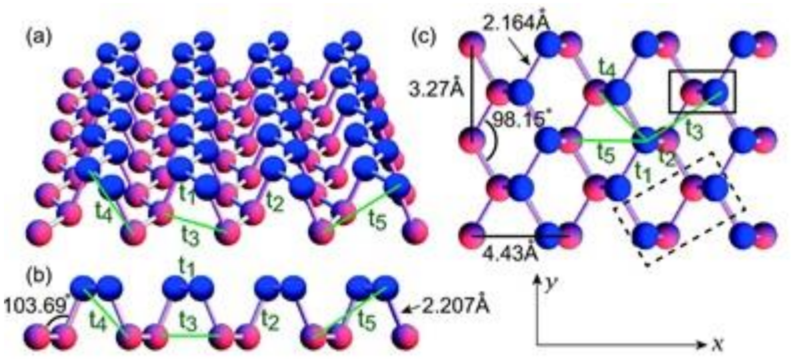

Fig. 5 Density of states (DOS) for $t_2=2|t_1|$.

4. Spectral Function

By using the full hamiltonianof the system, Green function can be obtained using equation[16]

$$G(K,\omega_n)=(Z-H)^{-1} \tag{4}$$

In this equation Z is defined as $Z=(\omega_n-i\eta)^{-1}$ and $\omega_n=\frac{(2n+1)\pi}{\beta}$ are Matsubara frequencies for fermions.

In the presences of these frequencies temperature should be added to the calculations. The temperature is considered $T = 0.01$□c. spectral function is defined like the equation

$$A(K,\omega_n)=-\frac{1}{\pi}\mathrm{Im}G(k,\omega_n)\ . \tag{5}$$

Spectral function for case 1 ($t_2=2|t_1|$) has been shown in Fig. (4) In this figure points with more density of state have greater spectral value (A). if all states are N, density of states (DOS) can be fined from equation

$$\rho(\omega_n)=-\frac{1}{N}\sum_K A(k,\omega_n) \tag{6}$$

It can be concluded from equation (6) that spectral function plays the role of local density of states. In figure 5 density of state for phosphorene for $t_2=2|t_1|$ has been shown.

As it is expected from Fig. 3 (a) density of states (DOS) in Fig. 5 shows conductor phase for phosphorene when $t_2=2|t_1|$. The reason for this conclusion is that there are two peaks in Fig. 5 for $\omega = 0$ which are not completely separated from each other.

5. Conclusion

Phosphorene is known as a semiconductor material which has a gap in its band structure. When tension is applied on phosphorene lattice Hamiltonian parameters of its lattice varies. In other words, when electrochemical pressure on material in specific direction increases, hopping parameters may increase. In this paper by considering t_1 parameter as a constant, t_2 parameter is considered as an independent parameter and gap changes can be studied. it is observed that by decreasing the ratio of t_2/t_1 from 3 for isotropic phosphorene, band gap gradually decreases until it disappears for t_2/t_1 and the material transfers to metal phase. For this case (t_2/t_1=2) a dirac point is observed in band structure which leads to the carrier mobility of phosphorene. Therefore, phosphorene can have conductivity property when it is under tension. These results show that phosphorene can be used for making electronic and industrial pieces when a material as a conductor in the presence of pressure is required.

Refrence

[1] K.S. Novoselov, A. Morozov, S. Jiang, D. Grigorieva, M. K. Dubonos and S. Firsov, Two-Dimensional Gas of Massless Dirac Fermions in Graphene. Nature 2005, 438, 197 −200.

[2] K. S. Novoselov, E. McCann, S. Morozov, V. Fal'ko, M. Katsnelson, U. Zeitler, D. Jiang, F. Schedin and A. Geim, Unconventional Quantum Hall Effect and Berry's Phase of 2π in Graphene. Nat. Phys. (2006), 2, 177 −180.

[3] K. F. Mak, C. Lee, Hone, J. Shan and T. F. Heinz, Atomically Thin MoS2: A New Direct-Gap Semiconductor. Phys. Rev. Lett. (2010),105, 136805.

[4]M. Ezawa, New Journal of Physics 16 (2014) 115004.

[5] A. Morita, Appl. Phys. A **39**, 227 (1986).

[6] L. Li, Y. Yu, G. J. Ye, Q. Ge, X. Ou, H. Wu, D. Feng,X. H. Chen, and Y. Zhang, Nature Nanotechnology **9**,372 (2014).

[7] S. P. Koenig, R. A. Doganov, H. Schmidt, A. H. C. Neto, and B. Oezyilmaz, Appl. Phys. Lett. **104**, 103106 (2014).

[8] W. Lu, et al., Nano Res. **7**, 853 (2014).

[9] J. Qiao, X. Kong, Z.-X. Hu, F. Yang and W. Ji, Nature Communications, 2014, **5**, 4475.

[10] E. Taghizadeh, M. Zare, and Fazileh, F., "*Scaling laws for band gaps of phosphorene nanoribb ons: A tight-binding calculation*", Physical Review B 91, 085409 (2015).

[11] M. Buscema, D. J. Groenendijk, S. I. Blanter, G. A. Steele, H. S. J. van der Zant and A. Castellanos-Gomez,Nano Lett., (2014), **14**, 3347–3352.

[12] Z. Wang, H. Jia, X. Zheng, R. Yang, Z. Wang, G. Ye, C. X. H, J. Shan and P. Feng, Nanoscale, (2014), DOI:10.1039/C1034NR04829F.

[13] A. Castellanos-Gomez, L. Vicarelli, E. Prada, J. O. Island, K. L. Narasimha-Acharya, S. I. Blanter, D. J. Groenendijk, M. Buscema, G. A. Steele, J. V. Alvarez, H. W. Zandbergen, J. J. Palacios, and H. S. J. van der Zant, 2D Materials **1**, 025001 (2014).
[14] A. N. Rudenko and M. I. Katsnelson, Phys. Rev. B **89**,201408 (2014).
[15] V. M Pereira, A. H. Neto, and N. M. R. Peres, Phys. Rev. B **80**, 045401(2009).
[16] H. Bruus, F. Karsten, *Many-body quantum theory in condensed ma tter physic*, Published by Oxford Graduate Texts(2004).