Electronic Structures of Thin Films of Black Phosphorus

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How the different thickness of thin films of black-P has an effect on its electronic band structure and structure has been studied by using SIESTA code. Although the interaction between the thin films has something to do with band reduction, it does not affect the inter-atomic distance between two nearest neighbour puckered layers.

INTRODUCTION

Black phosphorus (black-P) has presented a lot of benefits as an anode material for lithium ion batteries because of its atomic and electronic properties [1]. Consisting of puckered layers, black-P can guarantee enough capacity for lithium ion batteries. The Van der Waals interaction is known to be the major source of inter-layer coupling, causing a small band gap (0.19eV) [2]. However, the variation of energy band gap with the number of the puckered layers has not been understood yet, and an *ab initio* study is needed to get a reliable knowledge on the electronic properties of black-P thin films.

In this paper, we have investigated how the interaction between adjacent puckered layers has an effect on the band structure of black-P, especially band gap at the Γ point, by varying the number of the puckered layers.

COMPUTATIONAL METHODS

We have investigated the electronic band structure of the thin films of black-P by using density functional theory (DFT) calculations. We employed SIESTA code as implemented on the EDISON nanophysics web site [3]. Troullier-Martins norm-conserving pseudopotential was applied with the generalized gradient approximation (GGA) [4]. For the atomic relaxation, we used the kinetic energy cut-off of 300 Ry and 20x8x16 k-point mesh . A basis set of atomic orbitals following Sankey and Niklewski [5] were used.

RESULTS and DISCUSSION

Black-P is favorable in normal conditions than those of other allotropic forms such as white phosphorus (WP) and red phosphorus (RP). The bulk black-P has an orthorhombic symmetry with eight P atoms in a unit cell making a puckered layer structure, as shown in Fig.1, similar to that of graphine when it comes to the interaction among layers. A single puckered layer is designated by orange color in Fig.1, which will be called 1 bilayer (BL) since four P atoms are placed on the two planes, two in upper plane and two in lower plane. On each plane, two P atoms constitute a zigzag chain structure. Each atom composing a single BL has covalent bondings with three nearest neighbors (two on the same plane and one on the neighboring plane), keeping their bond lengths almost the same around 2.22 Å. The distance between two adjacent BLs (the yellow and the orange BLs in Fig.1) is known to be about 2.24 Å, which is slightly longer than that of the P-P covalent bond [2].

The band structure of 1 BL, 2 BL, 3BL, 4BL, and 5BL thin films are shown in Fig.2(a), where the energy is referred to the valence band maximun. While these band structures generally show similar features, the band gap at the Γ point is reduced considerably. As the number of puckered layers increases, the band gap tends to gradually decrease as shown in Fig.2(b). The biggest reduction occurs in the 2BL thin film with respect to the 1 BL case by 0.42 eV. Increasing the number of puckered layers to infinity corresponds to the bulk black-P, and the band gap of bulk black-P is expected to diminish. In fact, the conventional DFT calculations predicted the gapless electronic band structure, and the use of hybrid functional is known to reproduce small band gap at the Γ point [2].

To investigate how interaction among puckered layers has an influence on their structures, the bonding length between two P atoms on different

planes and both puckered layers were examined in Table.1. The bond length of P atoms lying on two adjacent planes within the same puckered layer remains the same as 2.124 Å and among the the BLs keeps 3.116 Å when adding the puckered layer one by one. Even though the interaction among BLs affects on the band gap size, it has nothing to do with the change in the structure of those puckered layers.

CONCLUSION

In conclusion, the tendency of a significant alteration in the electronic structure of thin films of black-P has been studied by using SIESTA code. As the number of puckered layers increases, the band gap at the Γ point decreases monotonically. The band gap almost vanishes when the thickness of thin films corresponds to 5 BLs. This suggests that the thickness of black-P has a great impact on the electronic properties due to the significant interaction between puckered layers. In addition, such strong correlation between the thin film thickness and the electronic structure of black-P open up the controllability of electronic properties such as the conductivity so that black-P can be the best material for lithium ion batteries.

FUTURE WORK

Although interaction among the puckered layers has something to do with the electronic structure of thin film, it does not lead to any variation in its structure such as bond length between two planes consisting of a single puckered layer as well as the inter-atomic distance between two nearest neighbour puckered layers. To figure out what causes the interaction related to the band gap reduction when the number of puckered layers increases, the relation between the charge density distribution and the thickness of the thin film needs to be investigated more thoroughly.

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REFERENCES

[1] Y. Du, J. Appl. Phys. **107**, 093718 (2010).
[2] A. Morita, Appl. Phys. **A 39**, 227-242 (1986).
[3] http://nano.edison.re.kr.
[4] J. P. Perdew, K. Burke, and M. Ernzerhof, Phys. Rev. Lett. **77**, 3865 (1996).
[5] A. Hübsch, Phys. Rev. Lett. **96**, 196401 (2006).

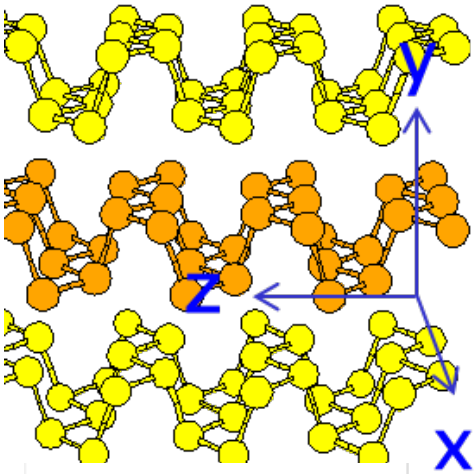
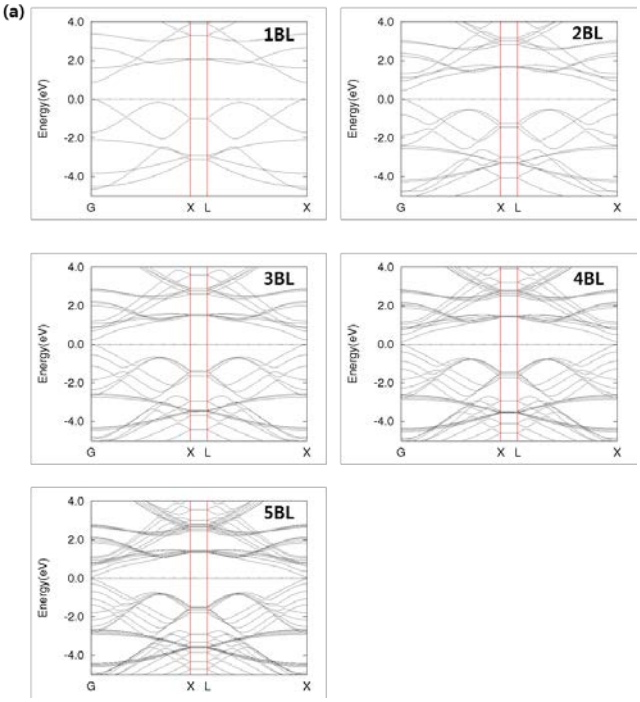
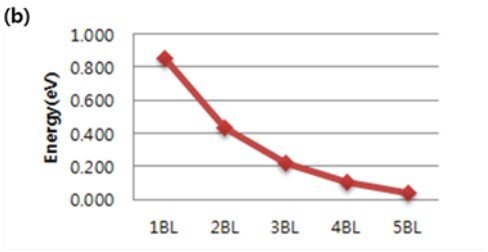


Fig. 1. Puckered layers of black-P.

	1BL	2BL	3BL	4BL	5BL
1BL	2.124	2.124	2.124	2.124	2.124
2BL		2.124	2.124	2.124	2.124
3BL			2.124	2.124	2.124
4BL				2.124	2.124
5BL					2.124
Δ(1BL-2BL)		3.116	3.116	3.116	3.116
Δ(2BL-3BL)			3.116	3.116	3.116
Δ(3BL-4BL)				3.116	3.116
Δ(4BL-5BL)					3.116

Table.1. Bonding length along with different numbers of puckered layers: The upper table represents the bonding length between two P atoms on the different planes within the same puckered bi-layer. The lower one shows the length between two adjacent bi-layers.





	band gap (eV)	Δgap (eV)
1BL	0.85	
2BL	0.43	0.42
3BL	0.22	0.21
4BL	0.11	0.11
5BL	0.04	0.07

Fig. 2. (a) Band structures of the different thin films of black-P: a single puckered layer (1BL), two puckered layers (2BL), three puckered layers (3BL), four puckered layers (4BL), five puckered layers (5BL). (b) Change of the band gap at the Γ point with the thickness of thin films.