Computational Materials Science 156 (2019) 292–300

Contents lists available at ScienceDirect

Computational Materials Science

journal homepage: www.elsevier.com/locate/commatsci

Effect of C and O dopant atoms on the electronic properties of black phosphorus nanotubes

Xinyue Dai, Lishu Zhang, Zhichao Wang, Jie Li, Hui Li*

Key Laboratory for Liquid-Solid Structural Evolution and Processing of Materials, Ministry of Education, Shandong University, Jinan 250061, People's Republic of China

ARTICLE INFO

Keywords:
Black phosphorus nanotubes
Transport property
Negative differential resistance

ABSTRACT

The electronic structures of the C and O-doped black phosphorene are investigated theoretically by using first-principles density functional theory (DFT). The results show that they are all metallic. And the black phosphorus nanotubes (BPNTs) rolled from the pure, C-doped and O-doped black phosphorene with different radii and chiralities are also studied. C and O atoms substitute for P atoms enable the armchair BPNT to have a metallic feature with several bands cross the Fermi level. Surprisingly, the number of the bands cross the Fermi level just equals the number of dopant atoms. But for the zigzag BPNT, when the O atoms decrease to 4, no band crosses the Fermi level and at which a minimal energy gap appears. Furthermore, the transport properties of two-probe devices fabricated by the pure A24 and Z34 BPNTs together with the C-doped A24 BPNTs are investigated theoretically. These calculated results show that the electronic transport properties of the A24 BPNT can be significant changed by C dopant atom and vary with the number of the doped atoms. The current-voltage curves of these BPNTs with C atoms substitute for P atoms present sinusoidal characteristics under low bias and negative differential resistance (NDR) properties. This study provides an effective route for tuning the electronic structures of black phosphorene and BPNTs and thus the transport properties of their electronic devices. And the unique properties of these black phosphorene and BPNTs also offer an inspiration for their subsequent experiments.

1. Introduction

With the development of electronic device miniaturization, the search for a new available low-dimensional material becomes more and more urgent. Black phosphorene, a novel two-dimensional (2D) atomic-layer material, has attracted tremendous attention owing to its high carrier mobility and immense application potentials in the field of optoelectronic devices [1,2]. And few-layer phosphorene has been exfoliated from bulk black phosphorus (BP) successfully [1–3], which further promoted the study on the black phosphene [4–7] and its derivative structures, such as nanoribbons [3,8] and nanotubes [9,10].

Similar to the carbon nanotubes (CNTs), which can be seen as the one-dimensional (1D) carbon materials curled from the graphene [11,12], the BPNTs rolled from the black phosphorene have been proposed recently and their electronic structure, optical properties, thermal properties and stability have been studied widely [13–18]. Seifert et al. [13] reported that the BPNTs rolled from the black phosphorene with diameters above 12.5 Å are stable. Afterward, using density functional theory (DFT) calculations, Cabria et al. [14] suggested that the single-walled phosphorus nanotubes are more stable than the corresponding strips and showed the possibility of synthesis of phosphorus nanotubes. But the structures of these BPNTs used in the early studies are actually blue phosphorus nanotubes (Blue PNTs) [15,19]. More importantly, Guo et al. [20] have made a great step forward in this field and found that BPNTs are direct gap semiconductors affected by the tensile strain and transverse electric field, regardless of their chirality. Cai et al. [19] investigated the thermal vibration of atoms on the stability of BPNTs using molecular dynamics method, and showed that BPNTs could work at a lower temperature. Subsequently, they studied the strength and stability of a BPNT under compression and found that BPNT with lower axial strain can still be stable at a higher temperature [20]. Much work has also confirmed the structural stability of the BPNTs rolled from the black phosphorene with larger diameters or at a lower temperature [16,21,23,24]. Sorkin and Zhang [17,18] studied the mechanical properties of BPNTs and found that their deformation and failure are anisotropic and divacancies in AC PNTs, monovacancies in ZZ PNTs possess the lowest vacancy formation energy, which decreases with the tube diameter in AC PNTs and increases in ZZ PNTs. These discoveries provide guidelines for the design BPNT nanodevices.

---

* Corresponding author.
E-mail address: lihuilmy@hotmail.com (H. Li).

https://doi.org/10.1016/j.commatsci.2018.09.059
Received 27 July 2018; Received in revised form 6 September 2018; Accepted 17 September 2018

Despite these great deals of theoretical efforts, there are still some unsolved problems regarding the black phosphorene and the single wall black phosphorus nanotubes (SWBPNTs) derived from it. For example, the effect of vacant and dopant atoms on the electronic structures of these tubes are still lacking. Generally, the doping of the dopant atoms, such as C and O, was used to change the electronic structure of the black phosphene and modify its properties [25–29]. More significantly, however, controlling the electronic structures of nanomaterials is of great importance to their application in the optoelectronic field.

In order to explore how the dopant atoms affect the electronic and the transport properties of black phosphorene and BPNTs (rolled from it), we investigate the electronic structures of the C- and O-doped black phosphorene together with the pure, C-doped and O-doped BPNTs with different diameters and chiralities.

2. Computational method

The structure optimization of the pure and substitutional doped black phosphorene together with their electronic structure calculations are performed by using generalized gradient approximation (GGA) [30] with Perdew-Burke-Ernzerhof (PBE) [31] type parameterization based on density functional theory (DFT). Upon optimizations, the forces on all atoms are less than 0.05 eV/Å. All the large-diameter SWBPNTs are rolled from the optimized black phosphorene. The quantum electronic structures of these large-diameter BPNT unit cells are calculated using the self-consistent-charge density-functional tight-binding (SCC-DFTB) method [32–34] implemented in the ATK-Semi Empirical (ATKSE) Slater-Koster codes [35]. It is worth mentioning that DFT in GGA functional (such as the PBE functional) and the DFTB tend to underestimate the energy gaps. This may ultimately be attributed to their inherent lack of derivative discontinuity and delocalization error. Much effort has been devoted to resolve this problem, such as using the GW approximation or hybrid-DFT methods (such as HSE06). And the GW method yields a qualitatively correct trend toward the band gap opening, the HSE06 or GW results should be more reliable than the PBE to obtain the electronic and mechanical properties correct in phosphorene [36,37]. But the DFTB seems to be well suited for the treatment of the class of the large systems investigated in this work. The vacuum layers of the black phosphorene and BPNT supercells are set as 15 Å to avoid any interactions between the adjacent images. The density mesh cut-off for the electrostatic potentials is 75 Hartree. The electron temperature is set to 300 K. The 51 × 51 × 1 and 1 × 1 × 100 k points sampling in the Brillouin zone are used in 2D black phosphorene and 1D BPNT computations, respectively. And the electronic structures are analyzed by calculating their density of states (DOS), band structures and bloch states.

Non-equilibrium Green's Function (NEGF) and DFTB method are used to calculate the transport properties of two-probe devices composed of the single-wall BPNTs.

The device current I is described by the Landauer-Buttiker equation [38]:

$$I = \frac{2e}{h}\int_{-\infty}^{\infty} dE\,(T(E,\,V)(f_1(E)-f_2(E)))$$

where e and h are the electron charge and the planck constant respectively, $f_{1,2}(E)$ is the Fermi Dirac function of source and drain electrodes and $T(E,V)$ is the measure of probability of electrons transmit from the source to the drain contacts through the BPNT device which can be shown as:

$$T(E,\,V) = \mathrm{tr}(\Gamma_1 \mathrm{G} \Gamma_2 \mathrm{G}^{\dagger})$$

where G and $\mathrm{G}^{\dagger}$ are the retarded and advanced Green functions of the conductor part and Γ_2 and Γ_2 are the coupling functions to the left and right electrodes.

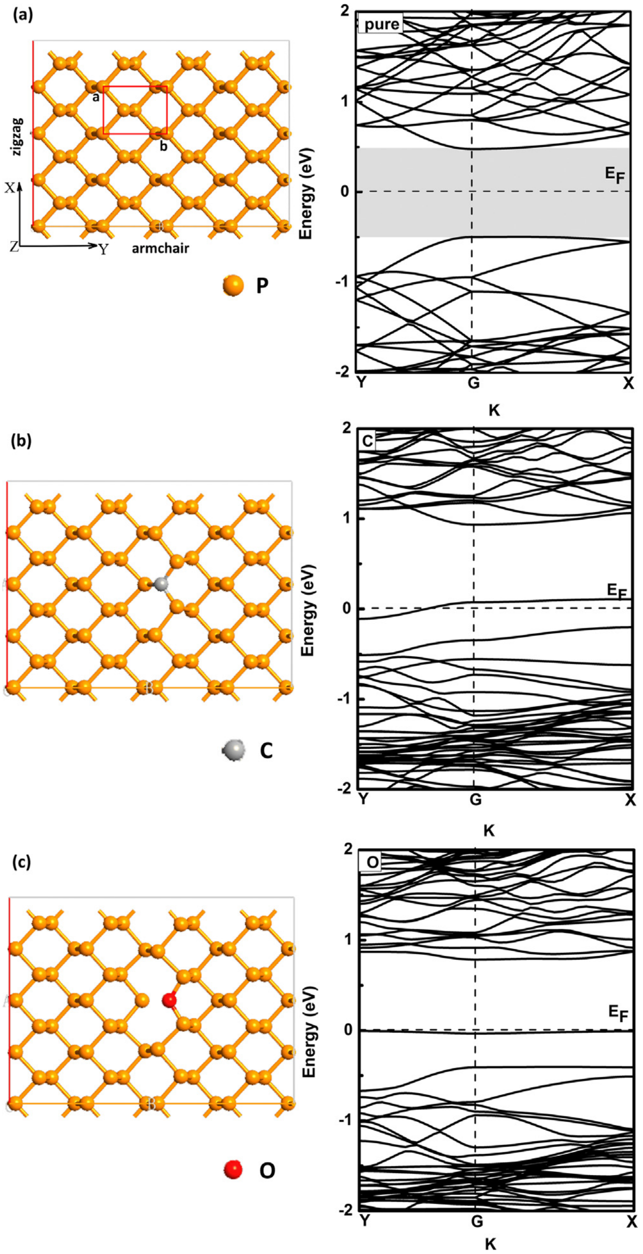

Fig. 1. Schematic illustrations and band structures of the (a) 2D black phosphorene, (b) C-doped and (c) O-doped black phosphorene with GGA-PBE functional. Y, G and X in the band structure correspond to the (0, 0.5, 0), (0, 0, 0) and (0.5, 0, 0) k-points, respectively, in the Brillouin-zone. The horizontal dashed line marks the Fermi level (the zero of the energy axis in these plots).

3. Results and discussion

The atomic structure of 2D black phosphorene is depicted in Fig. 1(a), the crystal structure is orthorhombic and the calculated lattice constants of the unit cell are a = 3.306 Å and b = 4.552 Å in the zigzag and armchair directions, respectively, in good agreement with the experimental value [39]. The P—P bond lengths are 2.22 and 2.26 Å. It can be drawn from the band structure that the pure black phosphorene is a semiconductor with a band gap of 0.98 eV based on GGA calculations, which is consistent with previous reports [6,40,41].

Moreover, dopant atoms are often unavoidable in 2D nanomaterials, and their electronic properties can be drastically altered by atomic doping. We thus calculate the band structures of the black phosphorene with vacancy and substitutional impurity atoms.