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Electric field and strain tunable electronic structures in monolayer Black Phosphorus

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ABSTRACT

Electric field or in-plane strain is used to tailor the electronic structures of monolayer Black Phosphorus (M-BP). Upon applying electric field, the band gap of M-BP is greatly reduced and insulator–metal transition happens under certain field intensity. The electric field impact on the electron effective mass (EEM) of M-BP is anisotropic. The EEM along armchair direction is increased and that in the zigzag direction is greatly reduced. Tensile strain under small magnitude enlarges the band gap of M-BP and starts to reduce it when the strain becomes relatively large. The anisotropic EEM in the M-BP can also be reversed by the tensile strain. Under tensile strain, the electronic structure of M-BP becomes to be more efficiently modulated by the electric field. Compression strain only reduces the band gap of M-BP and has little impact on the EEM. For the M-BP under compression strain, its electronic structure can hardly be altered by the electric field.

1. Introduction

Electric field or strain is the usually used ways to modulate the electronic structures of materials. Especially, in low dimensional systems, the quantum confinement effect makes their band structures be rather sensitive to the external electric field or the inductive strain [1–14]. Recently, ultrathin two dimensional materials have become the focus of scientific researches, inspired by the successful synthesis of the graphene in the experiments, which has exhibited extensively excellent properties [15–18]. Both in the experiment and in the theory, it has been demonstrated that, apart from graphene, other kinds of ultrathin materials also have numerous intrinsic outstanding properties and have great potential application in the future electronic or optical devices [19–23]. However, in some cases, the electronic structures of these two-dimensional materials cannot match the special requirements. For example, the zero band gap semi-metallic character greatly limits the use of graphene in field effect transistors, where relatively large on/off rate is required [15]. For hexagonal boron nitride (*h-BN*), on the other hand, its rather large band gap (~6.0 eV) has excluded its usage as the usual semiconductor materials [23]. Obviously, to extend the applications of two dimensional materials, effective ways that can tailor their electronic structures are deeply required.

Various methods have been proposed to effectively modulate the electronic structures of two dimensional systems. Among them, external electric field or strain, as mentioned above, attracts extensive attentions, because of their relatively easy applications in the actual operations and also their considerable modulation effects. For example, by breaking the inversion symmetry, external electronic field can effectively induce reversible band gaps in bilayer graphene [1,2,24]. When graphene is put on SiC substrate, small band gaps can be observed in it due to the in-plane strain arising from the lattice mismatch between them [25]. For multilayer hexagonal boron nitride (*h-BN*), on the other hand, its band gap can only be reduced by the vertical electric field [26]. In the two dimensional transition-metal dichalcogenides (TMDs), strain not only determines their band gap, but also impacts their magnetic ground states [27].

Black Phosphorus (BP) is the most stable configuration among all the allotropes of phosphorus atoms [28–30]. It is one kind of layer materials having structures that are quite similar to graphite. The phosphorus atoms in the layer are connected with each other through the covalent chemical bonds, and different layers are stacked together through the long range weak Van der Waals interactions. Because of such special configuration, multilayer or even single layer BP have been fabricated in the experiments, which are all kinds of the ultrathin two dimensional semiconductors with

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direct band gap in the appealing energy range [29]. Moreover, multilayer BPs has many unique features, such as the anisotropic electronic conductance, large carrier mobility, different optical response and the layer dependent electronic structures [28–38]. All of these distinguish this material from other layer semiconductors and make multilayer BPs have great potential use in the future electronic devices. However, in the actual application, the ultrathin BPs are put on the substrate material, which inevitably introduces in-plane strain in them due to the lattice mismatch. In addition, the non-uniform distribution of different kinds of atoms in actual devices will introduce electronic potential difference in the BPs. All the effects have great impacts on the electronic structures of the BPs, especially in the monolayer case. Moreover, for the ultrathin two dimensional materials, in-plane strain and electric field are also the usually used ways to control the carrier density and the on/off rate in the layer structures. Therefore, revealing the electronic structure response of the M-BP to the in-plane strain and the external electric field, not only helps to reveal the unique strain- and field-dependent electronic structures of the M-BP, but also contributes to its actual application in the electric devices.

Here, we report the electric field and strain effects on the electronic structures of M-BP. The band gap of M-BP can only be reduced by the vertical electric field. The EEM in M-BP is anisotropic with the one along the zigzag direction being larger than that in the armchair one. Under certain field strength, the direction-dependent EEM in M-BP is reversed and becomes just opposite to the pristine one. Both biaxial and uniaxial strain can efficiently tailor the band gap of M-BP, with the electronic structure of M-BP being more sensitive to the biaxial strain and the strain in the zigzag direction. Moreover, the tensile strain greatly impacts the EEM of M-BP and makes its electronic structure be rather sensitive to the external electric field. The compression strain, on the other hand, has little impact on the EEM of M-BP and makes its electronic structure be hardly changed by the electric field.

2. Computational methods

All the calculations of the total energy and the electronic properties are done based on the fully-electron methods with the application of the full potential Dmol3 code package [39,40]. The exchange–correlation energy was treated within the generalized gradieniet approximation (GGA), using the functional of Perdew, Burke, and Ernzerhof (PBE) [41], and a double numerical atomic orbital augmented by the d-polarization functions (DNP) is employed as the basis set. The M-BP is used as the structural model, which extends in the $\vec{x}$ $\vec{y}$ direction. The electric field is applied in the $\vec{z}$ direction and is vertical to the M-BP. Upon applying the electric field, there will be induced electric dipoles in the M-BP, which introduces long range interaction between M-BP and its neighbor images. To exclude such long range dipole–dipole interaction, the vacuum as large as 40 Å is applied in the $\vec{z}$ direction and also the dipole correction is adopted [42]. The effective mass is used to demonstrate the carrier mobility of M-BP along zigzag or armchair direction, approximately. The definition of the effective mass is: $\frac{1}{m^*} = \frac{1}{\hbar^2}\frac{\partial^2 E}{\partial k^2}$, where E is the energy and k is the wave vector along the transport direction. In all the calculations, the structure of the M-BP is fully relaxed with the convergence thresholds of 1×10^{-5} Ha for the energy, 1×10^{-3} Ha/Å for the force. The corresponding Brillouin zone is sampled in $8 \times 6 \times 1$ mesh using the Monkhorst–Pack scheme in the structural optimization, and $16 \times 12 \times 1$ mesh is used in the electronic structure calculations. The k points along the symmetry points (Fig. 1(a)) are selected to get the energy bands. In the self-consistent field calculations, the convergence threshold in the energy is chosen to be 1×10^{-6} Ha.

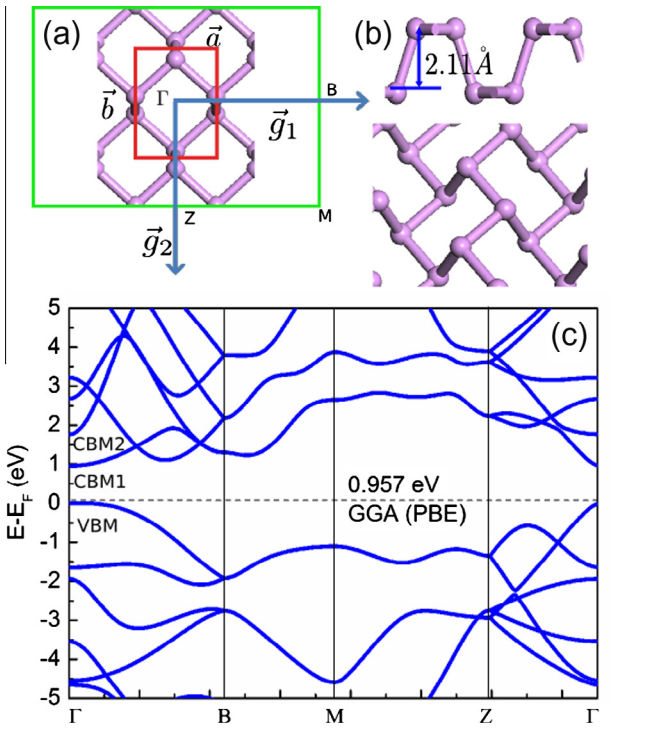

Fig. 1. (a) Top view of the structure of M-BP. The unit cell (red rectangle), the corresponding Brillouin zone (green-rectangle) and the high symmetry k points are marked out. (b) Side view of M-BP and the puckered distance. (c) The energy bands of M-BP, the valence band maximum (VBM), the first conduction band minimum (CBM1) and the second conduction band minimum (CBM2) are labeled out. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

3. Results and discussions

In Fig. 1(a and b), the configuration of M-BP is given, which is composed of the puckered hexagons and has the rectangular symmetry. The phosphorus atoms are connected with each other through the non-polar covalent bonds, and equally distribute on the two individual planes with the separation distance larger than 2 Å. The band structure in Fig. 1(c) demonstrates that M-BP is one kind of the direct band gap semiconductor with a 0.957 eV band gap locating at the Γ point. There are three kinds of the states around the Fermi level that are essentially important in determining the electronic properties of the M-BP. These states are the valence band maximum (VBM), the first conduction band minimum (CBM1) and the second conduction band minimum (CBM2). From these band dispersions, it can be got that the electron effective mass (EEM) in the M-BP is anisotropic. For the CBM1, the EEM in the zigzag direction is rather larger than that in the armchair direction. For the CBM2, on the other hand, the EEM along the armchair direction is quite large compared with that in the zigzag direction.

Because the configuration of M-BP is strongly puckered, its charge density can be easily redistributed by the vertical electric field. The electronic structure of M-BP is expected to be sensitive to the external electric field. The simulation results do show that, upon applying the vertical electric field, both the band gap and the EEM of M-BP can be effectively modulated. As demonstrated in Fig. 2(a), under relatively low electric field (<0.45 V/nm), the band gap and the EEM are almost unchanged. However, when the electric field reaches certain magnitude (~0.45 V/nm), the band gap of M-BP becomes to be linearly reduced. Insulator–metal transition occurs at relatively large electric field (0.8 V/nm). The EEM in the M-BP is anisotropic with the one along zigzag direction