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Electronic and optical properties of monolayer black phosphorus induced by bi-axial strain

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ABSTRACT

Black phosphorus (BP) is a new two-dimensional (2D) material. It has received significant attention because of its great potential in the field of optoelectronics, which arises due to its low-dimensional effects. In this paper, the effect of bi-axial strain on the band structure of monolayer BP has been studied by using the first-principles method based on density functional theory (DFT). We find that the band gap range of monolayer BP can be moderately and effectively adjusted by external stress from 0 to 1.845 eV. Simultaneously, the direct band gap is maintained during the stretching process, which leads to a high electron mobility suitable for applications. Moreover, the compressive strain can result in a semiconductor–metal transition (SMT) with few-layer BP, whereas tensile strain only affects the band gap. Based on the electronic properties of monolayer BP, its optical properties are analyzed in detail, and the influence of strain—from a compressive strain of 12% to a tensile strain of 12%—on these properties is systematically discussed. It is found that the strain range and mode have a significant impact on the optical properties. In addition, the dielectric function and absorption spectra calculated along two different directions indicate that a significant optical anisotropy appears, giving a strong directionality dependence in the primitive and strained monolayer BP. It can be concluded that by applying external stress to monolayer BP, its optical properties can be readily controlled, which is beneficial for device applications. Furthermore, based on its direction-dependent response to the external stress, this behavior can also be used to detect the orientation of the deposited BP without the need for precise electron microscopy.

1. Introduction

The discovery of the excellent physical properties of graphene [1] laid the foundation for many new fields of research. One of the most important fundamental requirements is to deepen the study of 2D atomic-layered systems. Such materials, such as hexagonal boron nitride (h-BN), transition metal dichalcogenides (TMDs), silene, germylene, and other 2D compounds, have attracted wide attention [2–5]. Graphene is well known for its many excellent properties, but the absence of a forbidden band is detrimental as the lack of a band gap generates only a small current-switching effect. However, a band gap is very important for semiconductor device applications such as solar cells and field-effect transistors, so its absence limits the application of graphene in practical components [6]. Therefore, the search for materials with a high carrier mobility and proper band gap has become a hot topic.

Black phosphorus (BP) has been studied since the 1950s [7]. It is a stable allotrope of phosphorus that is widely regarded as a graphene cousin, with a layered structure similar to graphite. The biggest difference from graphene is that BP is a semiconductor with a direct band gap; bulk BP has a band gap of 0.3 eV [8] while that of monolayer BP reaches 1.59 eV [9], and this material is more stable than silicon. Monolayer BP is a new type of 2D semiconductor material with a direct band gap that is favored by researchers because of its wide range of attributes, including its adjustable direct band gap, high carrier mobility, significant in-plane photoelectron anisotropy, and phonon properties.

By using density functional theory (DFT), Qiao and Wang et al. [10,11] demonstrated that the band gap of 2D BP depends on the number of layers: the band gap decreases with an increasing number of layers. The band gap reaches a maximum value of 1.59 eV when BP is reduced to a monolayer. A direct-indirect-direct transformation of the band gap occurs when uniaxial strain is applied to 2D BP, as reported by Peng et al. [12]. Ong et al. [13] reported that the strong thermal transport anisotropy and strain modulation in monolayer BP. In a recent theoretical study by Ouyang et al. [14] it was shown that the stress responses of monolayer BP show

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evident anisotropy due to different edge type structures. Li et al. [15] obtained several layers of BP by mechanical exfoliation, and fabricated field-effect transistors with a reliable transistor performance at room temperature. Recently, a multi-scale approach for the theoretical description of deformed phosphorene was presented by Midtvedt et al. [16]. Jiang et al. [17] also reported the elastic modulus and ultimate strain of single layer BP, and described in detail its anisotropic mechanical properties under tensile and compressive strains. Tailoring the electronic properties of semiconductor nanostructures has been critical for their applications. Strain has long been used to tune the electronic properties of semiconductors [12,18]. As a practical issue, strain is almost inevitable in fabricated monolayer nanostructures, which manifests as buckling and the formation of ridges [19]. A more interesting case comes from intentionally introduced and controlled strains. Methods for introducing strain include lattice mismatch, functional wrapping, material doping, and direct mechanical application [20]. However, considering these previous studies, a full and detailed systematic analysis of the effect of strain on the band structure of BP is still missing. Therefore, it is of great practical significance to conduct a comprehensive and systematic study of the photoelectric properties of the system by using accurate calculation methods. This article will provide a full analysis of the effect of strain on the band structure and optical properties of monolayer BP.

The first-principles method has been widely applied in varied studies on the photoelectric properties of materials. In this work, all calculations were performed using the Cambridge Sequential Total Energy Package (CASTEP) code based on the primary principle of plane wave turns potential method. Given that BP is a semiconductor material with a tunable band gap, the use of this and other 2D materials in practical applications often needs to consider the interfacial contact stress problems. In this paper, the band gap is modified by applying external stress to the system, and the adjustable range and responses of monolayer BP are studied systematically. The effects of bi-axial strain on the band structure and optical properties of monolayer BP crystals are discussed in detail, including the trends of these properties with strain. It is hoped that the results will provide a useful theoretical basis for the experimental research on and application of BP crystal materials in optoelectronic devices.

2. Simulation details

BP is one of the most stable allotropes of phosphorus. The bulk BP material possesses a lamellar structure, similar to graphite. Fig. 1(a) shows a model of the perfect crystal structure of bulk BP, which is orthorhombic with a *Cmca* space group and eight P atoms in each unit cell. The experimental [21] lattice parameters are $a = 3.313$ Å, $b = 10.473$ Å, and $c = 4.374$ Å, and the crystal plane angles are $\alpha = \beta = \gamma = 90°$. The crystal structure of BP is different from that of graphene as it consists of folded layers of P atoms, and each P atom is connected to three others by short covalent bonds. This structure ensures that the properties of BP are more stable than those of red phosphorus and white phosphorus. The crystal structure of monolayer BP was obtained by isolating a layer from bulk BP, as shown in Fig. 1(b).

The calculations are performed by using DFT with the generalized gradient approximation (GGA) implemented in CASTEP, and using Vanderbilt-type ultra-soft pseudo-potentials for the electron–ion interactions. Periodic boundary conditions are used in this calculation process. The exchange-correlation potential of Ceperley and Alder as parameterized by Perdew and Zunger (CAPZ) [22] in the local density approximation (LDA) were used, along with the GGA schemes of Perdew and Wang (PW91) [23] and Per dew–Burke–Ernzerhof (PBE) [24]. In particular, different DFT-D approaches to treat the van der Waals (vdW) interactions were employed, notably the Ortmann, Bechstedt, and Schmidt (OBS) [25] correction to PW91, as well as the Tkatchenko and Scheffler (TS) [26] and Grimme [27] corrections to PBE. These methods have been shown to be reliable and are often used for electronic structure calculations [28–30]. Accordingly, in this work, the above-mentioned methods are employed to describe the electronic exchange-correlation potential. In the subsequent calculations of the band structure, density of states, and optical properties of this system, since the PBE exchange-correlation functional often underestimates the band gap, the more accurate hybrid Heyd–Scuseria–Ernzerhof (HSE06) [31] functional was used; the norm-conserving pseudo-potential was chosen because it is more accurate than the ultra-soft pseudo-potential in optical calculations [32].

Before starting the simulation work, the convergence test and geometric optimization of the BP cell are first performed. The test results are shown in Fig. 2. The kinetic energy cutoff for the plane wave basis set was chosen to be 500 eV. For the bulk BP cell, the reciprocal space was meshed at $8 \times 10 \times 4$ using the Monkhorst–Pack method. For single layer BP thin film K-point grid, the Brillouin zone integrations are performed using a Monkhorst–Pack grid of $8 \times 10 \times 1$ for relaxation. The total energy until convergence obtained during the structure optimization was less than 10^{-6} eV/atom, and all of the structure models were fully relaxed until the forces were less than 0.01 eV/Å, per the convergence criterion.

3. Results and discussion

3.1. Geometric structure optimization

The theoretical equilibrium crystal structure was obtained by full structural optimization using LDA, GGA, and three versions of GGA-D. The calculated structural parameters are presented in Table 1. Taking the experimental cell volume as the theoretical reference, we find the differences between the calculated and experimental measured volumes to be 11.07% with LDA, 8.77% with PW91, and 10.0% with PBE. These large errors indicate that the exchange-correlation potential does not capture the intermolecular interactions in BP accurately. However, the calculated results found with the three DFT-D methods were in good agreement with the experimental values, with the errors in the predicted equilibrium volumes being only 1.55%, 2.92%, and 0.51%, respectively, for the PW91-OBS, PBE-TS, and PBE-Grimme parametrizations. Considering the three lattice parameters, it is obvious that the maximum error is found for *b*, the parameter lying perpendicular to the BP layers along the *z*-direction. Consequently, dispersive forces play a dominant role in the interlayer interactions, and considering this type of interaction is very important to provide an accurate description. The lattice constants of *a*, *b*, and *c*, along with the unit cell volume, were calculated by the GGA-PBE-Grimme method with relative errors of 0.48%, 0.53%, 0.53%, and 0.51%, respectively. These are the minimum errors obtained of all the methods, and the system essentially keeps the original structure. These findings show that the overall results obtained by the GGA-PBE-Grimme method were in good agreement with the experimentally measured values. The model and calculation method used in this paper were reasonable and reliable, and gave highly accurate results.

3.2. Electronic properties

In condensed matter physics, the band theory of solids is the fundamental concept used in understanding the physical and electronic properties of materials, such as conductivity, thermal