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Electronic and optical properties of bilayer blue phosphorus

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ABSTRACT

We investigate the electronic and optical properties of monolayer and stacking dependent bilayer blue phosphorus in the framework of density functional theory (DFT) and tight-binding approximations. We extract the hopping parameters of TB Hamiltonian for monolayer and bilayer blue phosphorus by using the DFT results. The variation of energy band gap with applied external electric field for two different stacks of bilayer blue phosphorus are also shown. We examine the linear response of the systems due to the external electromagnetic radiation in terms of the dielectric functions in the DFT theory. The relatively large electronic band gap and possibility of exfoliation form bulk structure due to weak interlayer coupling, make blue phosphorus an appropriate candidate for future electronic devices.

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1. Introduction

After the discovery of graphene [1], other 2D nano-structures were predicted theoretically [2–4] and synthesized in laboratory [5–7]. Among these, the monolayer black phosphorus, 2D puckered structure of phosphorus, which was also successfully fabricated in laboratory [8,9] and studied with several theoretical works [10–16]. Moreover, another 2D structure of phosphorus with A7 phase which is known as blue phosphorus, is confirmed to be as stable as 2D black phosphorus due to the absence of imaginary frequencies in phonon spectrum [17–19]. In the meanwhile, there are few number of theoretical studies on buckled structure of phosphorus [19–21]. Also it was shown the blue phosphorus is stable under substitution of light non-magnetic atoms [22]. Recently the quantum spin-Hall states have been predicted in bilayer black phosphorus [23]. The carbon atoms in the graphene have sp^2 hybridization which leads to in-plane σ and an out-of-plane π states in graphene plane. In the case of phosphorus the hybridization is sp^3 which is caused by the extra valence electron. The sp^3 hybridization leads to the out-of-plane atomic position and the buckled structure in phosphorus 2D nano structures [24]. The electronic band in graphene are mostly arised from the atomic p_z orbital in the π states perpendicular to the graphene plane. As a result, the simple single tight-binding model works for low energy states around the Fermi level considerably

well. But for the sp^3 hybridization in phosphorus one should consider at least 4 atomic orbitals for an appropriate tight-binding model. From an experimental point of view the multilayer structures are more convenient in laboratory because of difficulty to obtain monolayer. In the bilayer and multilayer 2D nano-structures, number of layers and stacking may tune different physical properties. The electronic band gap is tunable by stacking in silicene [25,26]. The optical properties is also stacking dependent in graphene [27,28] and black phosphorus [29,30]. Due to the buckling atomic structure, the blue phosphorus has more possible stacking than the graphene. The bonding between layers due to the van der Waals interaction should be considered in the DFT-D model [31]. In the tight-binding calculations, the binding between layers is modeled by additional hopping between atoms. Here, we study the electronic and optical properties of monolayer and bilayer blue phosphorus. In the case of bilayer blue phosphorus we consider four different stacking of adjacent layers. For the electronic calculations from DFT and four atomic orbital tight-binding models were employed. Finally, the optical properties of monolayer and most stable bilayer structure are calculated based on DFT.

2. Model and method

We investigate the electronic properties of monolayer and bilayer blue phosphorus with different stacking in the DFT and tight-binding theories. We fit the DFT results with tight-binding model to obtain the required parameters which are applicable for future theoretical study of bilayer blue phosphorus.

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2.1. Density functional theory

In this work, all the first-principles calculations are performed by using VASP package [32]. The exchange correlation potential is approximated by generalized gradient approximation (GGA) with PBE [33,34]. A plane-wave basis set with kinetic energy cutoff of 500 eV is used. All atomic positions and lattice constants are optimized by using the conjugate gradient method with DFT-vdW [35]. Moreover, Brillouin zone sampling with Monkhorst–Pack method [36] of $24 \times 24 \times 1$ k-points and to eliminate the interaction between monolayers in supercell, ~ 30 Å vacuum were considered. The convergence for energy was set as 10^{-8} eV between two steps and the maximum Hellmann–Feynman forces acting on each atom was less than 0.001 eV/Å upon ionic relaxation.

2.2. Tight-binding calculations

In the tight-binding calculations we consider four atomic orbitals per phosphorus atom as the basis set. For monolayer the hopping between nearest-neighbor (NN) and next-nearest-neighbor (NNN) are included in the tight-binding Hamiltonian. In the case of bilayer the hopping between adjacent layers is also included in the Hamiltonian. To construct the total Hamiltonian the required Slater-Koster hopping parameters which include the on-site energy of s and p atomic orbitals, hopping parameter between nearest-neighbor t_{NN} and next-nearest-neighbor t_{NNN} atomic sites and layers are extracted by fitting the band structure with DFT results in the first Brillouin zone. The real space Hamiltonian matrix is Fourier transformed and diagonalized to find the electronic bands as a function of wave vector in the first Brillouin zone. Here, all tight-binding calculations are performed by using a self-developed code.

2.3. Optical properties

To learn more about the technological importance of these structures, we focus our attention on optical properties using GGA-PBE functional. The linear response of a system due to an external electromagnetic radiation is described by the complex dielectric function $\varepsilon(\omega) = \varepsilon_1(\omega) + i\varepsilon_2(\omega)$ [37]. The dispersion of the imaginary part of complex dielectric function $\varepsilon_2(\omega)$ was obtained from the momentum matrix elements between the occupied and unoccupied wave functions as follows:

$$\varepsilon_2^{(\alpha\beta)} = \frac{4\pi^2 e^2}{\Omega} \lim_{q \to 0} \frac{1}{q^2} \sum_{c,v,\mathbf{k}} 2\omega_{\mathbf{k}} \delta(\epsilon_{c\mathbf{k}} - \epsilon_{v\mathbf{k}} - \omega) \times \langle u_{c+\mathbf{k}+\mathbf{e}_{\alpha q}} \mid u_{v\mathbf{k}} \rangle \langle u_{c+\mathbf{k}+\mathbf{e}_{\alpha q}} \mid u_{v\mathbf{k}} \rangle^*$$

(1)

where the c and v correspond to conduction and valence band states respectively, and $u_{c\mathbf{k}}$ is the cell periodic part of the orbitals at the k-point $\mathbf{k}$. The real component of the dielectric function, $\varepsilon_1(\omega)$ is calculated via the KramersKronig transformation [38]. Then, other important optical constants such as the reflectivity $R(\omega)$, the electron energy-loss spectrum $L(\omega)$, as well as the refractive index $n(\omega)$, and the extinction coefficient $k(\omega)$ were calculated using the following expressions [39,40]:

$$R(\omega) = \left| \frac{\sqrt{\varepsilon(\omega)} - 1}{\sqrt{\varepsilon(\omega)} + 1} \right|^2, \quad L(\omega) = \left(\frac{\varepsilon_2(\omega)}{\varepsilon_1^2(\omega) + \varepsilon_2^2(\omega)} \right)$$

$$n(\omega) = \left(\frac{\sqrt{\varepsilon_1^2(\omega) + \varepsilon_2^2(\omega)} + \varepsilon_1(\omega)}{2} \right)^{1/2},$$

(2)

$$k(\omega) = \left(\frac{\sqrt{\varepsilon_1^2(\omega) + \varepsilon_2^2(\omega)} - \varepsilon_1(\omega)}{2} \right)^{1/2}.$$

3. Results and discussions

The monolayer blue phosphorus consists two different sub-lattices that are separated by the buckling length as shown in Fig. 1. The buckling length for monolayer is 1.23 Å which is comparable with previous reports [21] and stanene buckling length [3]. All the structural parameters have also shown in Table 1. The electronic band structure in the DFT and tight-binding models and partial density of states (PDOS) are plotted in Fig. 2 for monolayer. The monolayer blue phosphorus is a semiconductor with indirect gap. The valence band maximum (VBM) and conduction band minimum (CBM) are between Γ-K and Γ-M in the first Brillouin zone, respectively. The gap value is 1.94 eV for DFT which is in fair agreement with tight-binding band structure. Black/blue arrows show the position of VBM and CBM in DFT/tight-binding theories. According to the PDOS for different atomic orbitals, the main contribution around the Fermi level is related to the p atomic orbitals. Unlike the graphene, contribution of s atomic orbitals in the total density of states is not negligible which shows the importance of different hybridization of s and p atomic orbitals for tight-binding calculations.

For bilayer blue phosphorus we examined different stacks as shown in Fig. 1. In the AA stack (Fig. 1(b)) the second layer is exactly above the first one but in the AB stack (Fig. 1(c)) the upper layer is moved in xy plane with respect to the first layer. Due to the buckling, there are different atomic configurations for AB bilayer structure. The relaxation process for AB stack is started from different configurations to guarantee the global minimum energy for AB structure. We minimized the total internal atomic force and stress for all structures. According to our calculations of the AA and AB stack bilayer blue phosphorus have the minimum energy and considered as the most stable structures in the following. The inter-layer binding energy for AA and AB stacks is 25 meV (cohesive energy as 12.5 meV/atom) which is comparable for a typical van der Waals layered structure, such that cohesive energy of graphene-hexagonal boron nitride superlattices was found around ~ 9.5 meV/atom from GGA + vdW functional [41]. The weak binding between layers in bilayer blue phosphorus make it possible to exfoliate 2D layer from the bulk one. The inter-layer distance in bilayer structures are 3.24 and 3.21 Å for AA and AB stacks, respectively. Buckling parameter of bilayer is almost same as monolayer for blue phosphorus. Electronic band structure and PDOS of bilayer blue phosphorus plotted in Fig. 3 for AA and the stable AB stacks.

The position of VBM and CBM are hardly ever changed in the bilayer structure with respect to the monolayer but they move toward each other that decreases energy gap to ~ 1 eV. In the bilayer structures the atomic p orbital enter to the electronic gap region. Each energy band in the monolayer is split to two bands due the interaction between two adjacent layer. The fitting process between DFT and tight-binding is done in an iterative Monte Carlo method to obtain the best possible set of parameters. The difference between on-site energy of s and p atomic orbitals is -4.55 eV for monolayer and different type of bilayer structures of blue phosphorus. Table 2 contains all the tight-binding parameters required to construct the Hamiltonian for different structures. Our tight-binding parameters for monolayer blue phosphorous are in good agreement with Ref. [42]. Due to the simple atomic structure for the AA stack only nearest neighbor hopping leads to relatively good results but for AB configuration we consider both nearest neighbor and next nearest neighbor hopping integrals for bilayer blue phosphorous.

The PDOS for AA and AB stacks shows the contribution of s atomic orbitals in the total density of states in bilayer structure.

The tight-binding model predicts position and size of electronic band gap that is a remarkable success for a simple atomic-orbital