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Strain-induced band structure and mobility modulation in graphitic blue phosphorus

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ABSTRACT

The effects of external strain on the electronic structure and carrier mobility of graphitic blue phosphorus are investigated theoretically. Symmetry breaking induced by the in-plane strain not only modulates the band structure, but also changes the carrier population at the valence band maximum and conduction band minimum so that the transport current density can be regulated. Compressed deformation in the direction normal to the plane transforms the blue phosphorus into an in-plane structure and the superfluous electrons reduce the band gap giving rise to a semiconductor–metal transition. Our theoretical assessment reveals that strain engineering is a useful method to design electronic devices.

1. Introduction

Elemental phosphorus is stable as white, red, violet, blue, and black allotropes and its color is defined by the fundamental band gap [1,2]. The most stable one is black phosphorus which has recently attracted much attention because of its potential in high-performance electronic devices. Since black phosphorus has high anisotropic hole-dominated mobility [3–6], directional factors must be considered in the design of devices making it challenging to integrate into current manufacturing technology. In addition, the band gap of black phosphorus is 0.59–1.51 eV [4] and most visible light cannot be properly utilized by optoelectronic devices. Another stable allotrope with a wider band gap is blue phosphorus in which the in-plane hexagonal structure and bulk layer stacking are very similar to those in graphite [7] which has a wide fundamental band gap of more than 2 eV. Due to the weak interlayer interaction, blue phosphorus can be exfoliated easily to form quasi-two-dimensional (2D) structures and has promising applications in optoelectronics.

If the carrier mobility is high, blue phosphorus with a few layers is a contender in the emerging field of post-graphene 2D electronics. In a 2D structure, the carrier mobility is related to the band structure and hence, regulation of the band structure at the valence band maximum (VBM) and conduction band minimum (CBM) (valley position) is very important. External strain, which can be easily implemented by introducing a specific substrate during the fabrication of blue phosphorus devices, is an effective way to modulate the electronic structure and carrier mobility. In fact, if the effects of external strain on carrier mobility can be exploited, the transfer current can be controlled by strain engineering. However, our understanding of strain-dependent electronic structures and carrier mobility in blue phosphorus devices is still quite limited.

In this work, the relationship between external strain and carrier mobility in graphitic blue phosphorus is investigated theoretically. The results disclose that symmetry breaking induced by the in-plane strain not only regulates the band structure and carrier mobility, but also changes the carrier population at the valley. The carrier mobility and concentration alter the transport current density. Compressed deformation in the direction normal to the plane decreases the band gap and induces a semiconductor–metal transition.

2. Theoretical methods

The theoretical assessment is based on the density functional theory in the Perdew–Burke–Ernzerhof generalized gradient approximation using the Vienna *ab initio* simulation package (VASP) code with projector augmented wave pseudopotentials [8–10]. The plane-wave energy cutoff of 500 eV is used to expand the Kohn–Sham wave functions and relaxation is carried out until

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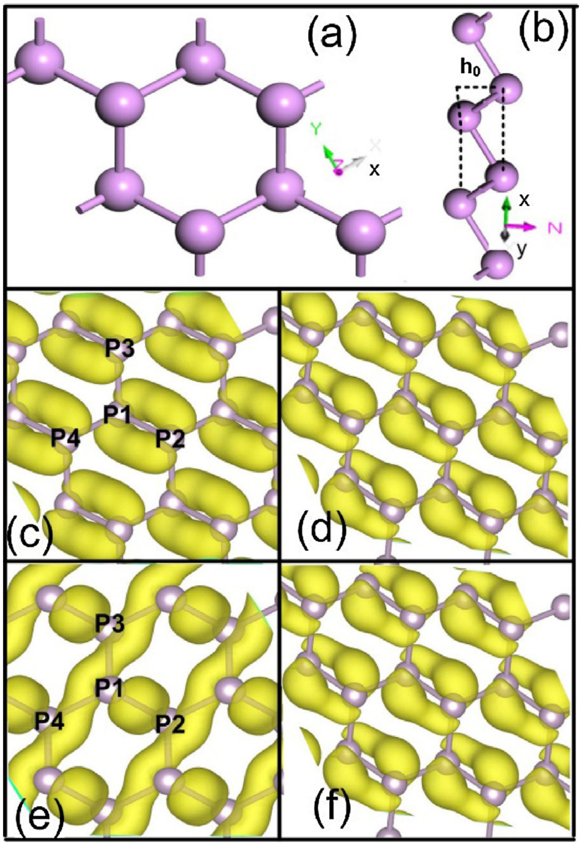

Fig. 1. (a) Top view and (b) side view of the (2 × 2) blue phosphorus monolayer; calculated electronic density of (1 × 1) blue phosphorus monolayer at VBM (c) and CBM (d) in the absence of strain; calculated electronic density of (1 × 1) blue phosphorus monolayer at VBM (e) and CBM (f) with 3% uniaxial strain along the *x* direction.

all forces on the free ions converge to 0.01 eV/Å. The vacuum space is at least 15 Å, which is large enough to avoid the interaction between periodical images. The Monkhorst-Pack *k*-points grid (10 × 10 × 1) has been tested to converge well. Moreover, since the standard density functional theory may fail to describe the band structure, state-of-the art hybrid functional calculation based on the Hey–Scuseria–Ernzerhof (HSE06) functional is adopted in this work [11].

3. Results and discussion

The optimized hexagonal (2 × 2) supercell of an isolated blue phosphorus monolayer with the 3.243 Å lattice constant is spanned by lattice vectors in the *x* and *y* directions (Fig. 1a). By considering the long-range van der Waals correction in the DFT-D2 methods [12], the influence of the interlayer interaction on the in-layer structure can be neglected because of the small change from $x = y = 3.240$ Å in the bulk to 3.3243 Å in the isolated monolayer. As shown in Fig. 1b, the side view of blue phosphorus displays an ideal in-layer connection by dislocation, and the relaxed thickness of the monolayer is 1.218 Å (marked by h_0). The electron density at VBM and CBM is evenly distributed among adjacent phosphorus atoms (P1—P2 bond) in the absence of external strain (Fig. 1c and d). When uniaxial strain is applied along the *x* direction (Fig. 1e and f), asymmetric deformation induced by the external strain breaks the intrinsic symmetry, which makes the electronic density at VBM deviate from the P1—P2 bond to P1—P3 and P1—P4 bond vicinity. However, asymmetric deformation induced by uniaxial strain cannot alter the electronic density distribution at CBM. The results demonstrate that the electronic density distribution at VBM is associated with structural deformation which can be exploited to regulate the band structure and carrier mobility.

For verification, the band gap of the (1 × 1) blue phosphorous monolayer with different in-plane strain and band structure along the high symmetry points are shown in Fig. 2a and the inset of Fig. 2b, respectively. In the absence of external strain ($xy = 0\%$), the calculated band structure shows that a blue phosphorus monolayer is semiconducting with an indirect band gap of 2.72 eV, which is close to that derived by the GW approach (2.62 eV). The results generated by the HSE06 method are adopted in this work, because they are more exact (the DFT band gap is underestimated to be 1.65 eV). As shown in Fig. 1c and d, the electron density associated with VBM and CBM is mostly dispersed at the P—P bond (not confined tightly to phosphorous atoms). Owing to the asymmetrical distribution, the VBM and CBM (valley position) deviate from the high symmetry points to be located between K–G (G–B) (marked by C1 and C2) and G–F (G–B) (marked by V1 and V2). Such a band structure indicates that the conduction/valence bands have two minima/maxima at equal energy but different momentum (marked by the red line). This provides the possibility to vary the electron quantity in each valley. Therefore, electronic devices can be designed by using the valley degree of freedom. Tensile deformation induced by biaxial strain ($xy = 3\%$) can reduce the CBM values (C1 and C2) (marked by the black line) and shift the VBM position (V1 and V2) slightly. Because the bond length is stretched to 2.274 Å ($xy = 3\%$) from 2.229 Å ($xy = 0\%$), symmetrical deformation reduces the overlapping of the electron wave function. Symmetry breaking induced by the uniaxial strain ($x = 3\%$) not only decreases C1 (keeping C2 constant), but also enlarges the discrepancy between V1 and V2 (VBM) to 0.11 eV ($xy = 3\%$) from 0.04 eV ($xy = 0\%$). The energy splitting between CBM (C1 and C2) and VBM (V1 and V2) adjusts the electron population at each valley thus playing a crucial role in the carrier injection and quantum transport.

To compare the structural stability, the formation energy is expressed as $E_f = E_r - E_0$, where E_r and E_0 represent the deformed energy and free energy. The maximum deformation energies are calculated to be 0.1453 eV ($x = 9\%$) and 0.1553 eV ($xy = 9\%$), and so the discussed strain range can be achieved without a large energy penalty. As shown in Fig. 2b, the band gap which depends on the applied in-plane strain is decreased to 1.4 eV ($xy = 9\%$) from 2.7 eV ($x = 0\%$). The possibility to change the band gap by ~50% in the strained geometries further suggests that strain-engineered blue phosphorus has potential applications in electronic devices. The obvious change in the band gap can be explained as follows: deformation induced by strain breaks the original balance and symmetry, and redistributes the electron wave function to form a metastable structure. Meanwhile, the atomic population is increased from 1.00 ($xy = 0\%$) to 1.03 ($xy = 9\%$) and s and p electrons are changed from 1.82 e and 3.18 e ($xy = 0\%$) to 1.84 e and 3.15 e ($xy = 9\%$).

As shown in Fig. 2c, compressed deformation [$z = (h - h_0)/h_0$, where h_0 is the thickness of the free layer] in the direction normal to the plane results in an in-plane expansion of the unit cell. The bonding structure of blue phosphorus is retained up to $z = 40\%$ and the structure of the strained materials approaches that of a puckered graphene layer. However, the CBM becomes as low as VBM marking the transition from indirect band gap semiconductor to metallic and it is related to the symmetry transformation from a beta structure to planar one. Fig. 2d shows the variation in the band gap until a point where the CBM descends below the VBM. In a narrow range of *z* between 30% and 35%, the deformed blue phosphorus displays a small density of state at the Fermi level and can be considered as a semi-metal. If there is more compression, the original valence band and conduction band finally cross ($z > 40\%$) deeply and the materials become metallic. The results indicate that the band structure and physical characteristics can be regulated by strain engineering.