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Electronic band structure of surface-doped black phosphorus

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ABSTRACT

We present an overview on the electronic band structure of surface-doped black phosphorus. Angle-resolved photoemission spectroscopy data show that the *in situ* deposition of potassium atoms on the surface of single-crystalline black phosphorus modulates the band gap in the wide range of 0.0–0.6 eV. At zero band gap, the surface layers of black phosphorus become a Dirac semimetal whose band dispersion is highly anisotropic, linear in armchair and quadratic in zigzag directions. In light of theoretical band calculations, we elucidate the mechanism of these band modifications as the giant Stark effect due to strong vertical electric fields induced by potassium atoms.

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1. Introduction

Over last few years, there has been growing interest in the study of two-dimensional (2D) crystals [1,2]. The confined electrons in reduced dimensions often give rise to new properties and functionalities that are not present in their bulk counterparts. The most widely studied 2D crystal is graphene, a single-layer of graphite. Graphene has rather a simple honeycomb lattice structure, and its charge carriers can be described by a pair of Dirac cones, the hallmark of effectively massless Dirac fermions [3–7]. This interesting low-energy band structure of graphene is responsible for a variety of remarkable properties, such as extremely high carrier mobility, Klein tunneling, and so forth. However, the lack of a band gap in graphene limits the current modulation in its field-effect transistors [8]. A recent research trend in the “post-graphene age” has shifted to searching for 2D crystals with an intrinsic and sizable band gap (that is, 2D van-der-Waals semiconductors), such as the 2*H* phase of transition-metal dichalcogenides and black phosphorus [9–12].

Black phosphorus (BP), the most stable allotrope of phosphorus, has been first synthesized by Bridgman about a hundred years ago [12–14]. BP has attracted renewed interest in recent years, as triggered by the successful exfoliation of BP thin flakes [15–21]. The initial works with the field-effect transistors of BP flakes demonstrated hole mobility as high as 1000 $\mathrm{cm}^2/\mathrm{V\,s}$ [15–17], and this value was theoretically predicted to increase up to 10,000 $\mathrm{cm}^2/\mathrm{V\,s}$ [22]. Indeed, the latter work with BP encapsulated by the double sheets of hexagonal boron nitrides has shown a higher carrier mobility of 6000 $\mathrm{cm}^2/\mathrm{V\,s}$, where the quantum Hall effect was clearly observed [23]. Furthermore, the previous studies have achieved the current modulation ratio of 10^5 at room temperature, which is much higher than that of graphene [12]. Owing to such promising device characteristics, BP has emerged as one of the 2D semiconductors with great potential for application in nanoscale electronic and opto-electronic devices [12,13].

The lattice structure of bulk BP consists of 2D van-der-Waals layers, similar to the relation of graphene and graphite. The single layer of BP is called phosphorene, where phosphorus atoms are arranged into a honeycomb network similar to graphene, but it is strongly modulated as shown in Fig. 1(a) to be armchair-shaped in the x direction and zigzag-shaped along the y direction (termed the puckered honeycomb structure) [24–30]. Each phosphorus atom has five valence electrons, two of which form a lone pair with an sp^3-like hybridization. The rest three make covalent bonds to neighboring three phosphorus atoms, leaving no unpaired electron in the unit cell. The low-energy band structure of phosphorene can be described by a bonding and anti-bonding pair of mainly p_z orbitals [24]. They correspond to the valence band (VB) and conduction band (CB), respectively, separated by a fairly large band gap of ~2.0 eV at the Γ point (Fig. 1(b)) [25–27]. This direct band gap together with its characteristic puckered structure gives rise to anisotropic properties of phosphorene, important for application in plasmonics and thermoelectronics [31,32].

For multilayers, two layers of phosphorene are stacked as a unit bilayer by weak van-der-Waals forces (relatively stronger than that of graphene layers). The introduction of finite interlayer coupling leads to the splitting of VB and CB along the interlayer direction (k_z), progressively reducing the magnitude of the band gap with increasing the number of layers [24–28]. In the bulk limit, the

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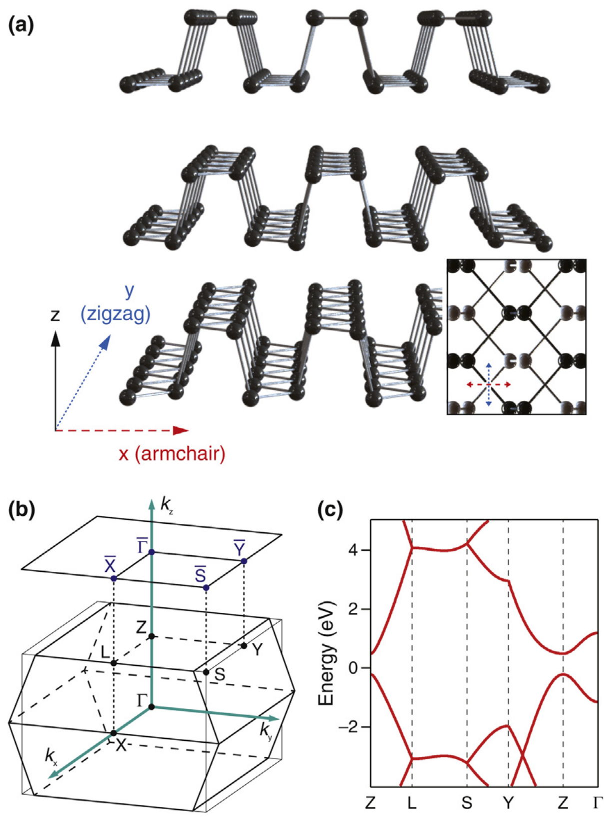

Fig. 1. (a) Puckered honeycomb (orthorhombic A17) structure of BP. Black balls and sticks represent phosphorus atoms and bonds. The principal axes are defined, as indicated in the bottom left. Inset is the top view to show AB stacking of phosphorene layers in BP. (b) Bulk and surface Brillouin zones. The high-symmetry points are marked with dots. (c) Theoretical band structure of bulk BP, obtained from the tight-binding model for the p_z orbital, as described in [25].

band gap is known to reach to 0.34 eV [24,25], where the finite k_z dispersion makes the VB maximum and the CB minimum to be located at the *Z* point of the bulk Brillouin zone (Fig. 1(b)). The band structure of bulk BP has been well established from the earlier experiments and theoretical model calculations, as shown in Fig. 1(c) [13–30].

As our understanding to the thin films of BP is being rapidly matured, a key issue is to modify and control the given electronic and optical properties of BP. The recent theoretical works have predicted that the puckered honeycomb structure of BP is highly susceptible to various physical parameters, such as stacking, strain, charge doping, and external fields [24–30,33–38]. In this paper, we present an overview of our angle-resolved photoemission spectroscopy (ARPES) studies on bulk BP doped by the *in situ* deposition of potassium (K) atoms [39]. We found that K atoms donate charges to adjacent surface phosphorene layers, which are confined to screen the ionized K atoms, leading to the formation of steep band bending. As a result, the band gap of BP is strongly modulated with the density of K atoms, providing an effective mechanism to modify the electronic and optical properties of BP.

2. Experiments

The ARPES measurements were conducted at the Beamline 4.0.3 (MERLIN) of the Advanced Light Source (ALS). This endstation is equipped with a R8000 electron analyzer (Scienta Omicron, Sweden). Energy and momentum resolutions were better than 20 meV and 0.02 Å^{-1}, respectively. Single-crystalline BP samples (Smart Elements and HQ Graphene) were cleaved in the ultrahigh vacuum chamber with the base pressure of 5×10^{-11} Torr. The linearly polarized synchrotron radiation was focused in the area of $100 \times 50\ \mu m^2$ to search for a best spot on the sample, where a signature of grain mixtures can be minimized. Most ARPES data were collected at the temperature of 15–25 K with the photon energy of $h\nu = 50$–120 eV. This range of photon energies was used to characterize the k_z dispersion of BP. The photon energy of 104 V was chosen for a *Z* point of the bulk Brillouin zone and even intensity distributions near the Fermi energy (E_F) [40]. The crystallographic direction of BP samples was checked by mapping the *k*-space band symmetry of ARPES spectra. The *in situ* deposition of K on the surface of BP was done by means of electrothermal heating of commercial K dispensers (SAES). A doping series of ARPES spectra was recorded by using a programmed sequence of depositions and measurements. The K 3*p* core-level spectra were simultaneously recorded to estimate the density of K dopants in units of monolayer (ML).

3. Results

Fig. 2(a) and (b) shows experimental ARPES spectra, taken for as-cleaved BP at the *Z* point along armchair (k_x) and zigzag (k_y) directions. As expected from theoretical band calculations, there is a well-defined VB of mostly p_z orbital located at the zone center. In Fig. 2(a), the ARPES spectral intensity taken at the first Brillouin zone is strongly suppressed in between ±0.01 Å^{-1} by the matrix-element effect, and the extreme of VB can be more precisely analyzed in Fig. 2(b), taken at the second Brillouin zone. The maximum energy of VB from E_F is variable for different samples in the range of 0.15 ± 0.03 eV. Considering the well-known band gap of bulk BP (0.34 eV), our samples are nearly charge-neutral or slightly hole-doped, consistent with the *p*-type conduction in transport measurements [41].

The band dispersion of VB is linear in Fig. 2(a) and nearly quadratic in Fig. 2(b). This armchair-zigzag anisotropic is a direct experimental confirmation for the highly anisotropic effective mass of bulk BP predicted in theoretical band calculations [26,30]. Furthermore, the ARPES spectral width is narrower in Fig. 2(a) than that in Fig. 2(b). Comparing momentum distribution curves (MDC) of ARPES spectra at −0.6 eV, we found that the full width at half maximum of VB in Fig. 2(b) is a factor of two greater than that in Fig. 2(a). This indicates a longer mean free path of hole carriers along the k_x axis, which explain the higher hole mobility along the armchair direction over the zigzag direction.

The evolution of this low-energy band structure is measured after the *in situ* deposition of K atoms on the surface of BP at 25 K. The adsorption of K atoms could be confirmed from the simultaneously taken K 3*p* core-level spectroscopy. We performed the curve fitting analysis after subtracting a smooth background taken from that of pristine BP. In Fig. 3(a), the K coverage on the surface of BP was estimated from the area of K 3*p* core-level peaks, which shows approximately a linear behavior with the deposition time. The characteristic shapes of K 3*p* core-level peaks are known for the K thin films, from which we extrapolate the K coverage at the lower density [42].

The K 3*p* core-level peaks show little dependence on the photon energy or a grazing sample angle (data not shown). This confirms that the deposited K atoms are adsorbed on the surface rather than being intercalated into subsurface layers. This picture can be further supported by recent density-functional-theory calculations demonstrating that the adsorption of K on the surface of BP is energetically favored over the intercalation [36]. The most stable adsorption site is shown in inset of Fig. 3(c), where the vertical distance between K and BP at equilibrium is found about 2.76 Å after relaxation. Furthermore, we found no signature of superperiodicity from ARPES spectra for the K coverage used in our experiments,

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