1. Introduction

In the past several years, two-dimensional (2D) materials with few layer atom thickness have been paid great attention due to their potential applications in electronics, optoelectronics, and energy conversion [1]. For instance, monolayer BN [2], MoS$_2$ [3–5] and Group IV monochalcogenides [6] are recently reported to possess large piezoelectricity [7] which would allow efficient mechanical-to-electrical energy conversion. Black phosphorene has been predicted to exhibit ferroelectricity [8], which has potential application for designing nonvolatile memory devices. In addition, $\delta$-P is predicted to be an auxetic material with a highly negative Poisson’s ratio [9]. Auxetic materials have also attracted intense research interest recently [10–12], since these materials possess some novel properties such as enhanced toughness and enhanced sound or vibration absorption [13]. Although 2D materials mentioned above usually possess outstanding properties, it’s temporarily hard to adapt multifunctional application. Therefore, in order to integrate multi-functionality in 2D semiconductor devices, 2D materials that hold simultaneously two or more primary properties or functions are highly desirable.

As a new class of 2D materials, boron-phosphorus binary compound semiconductors have gained great attention in recent years. In experimental aspect, several thin film growth methods for synthesizing B–P binary compounds have been proposed, including chemical vapor deposition (CVD) [14–16], close-spaced vapor transport (CVT) [17], flux growth [18], high pressure flux method [19], and epitaxy growth [20]. However, no experiment gave the clear structure information of layered B–P binary compounds. In theoretical aspect, all the studies [21–23] were prone to use the graphitic structure of boron-phosphide (g-BP) as the most stable phase, which may be wrong in reality. Therefore, a thorough investigation of the crystal structure of boron-phosphide will not only provide insight into the structure information of
experimentally synthesized B–P compounds, but also may lead to the discovery of new functional 2D materials.

In this work, we systematically predict the lowest-energy structures of 2D B–P compounds by using first principles simulation and variable components global optimization based on Cuttlefish algorithm [24], which is inspired by the mechanism of color changing behavior of the cuttlefish to find the optimal solution in numerical optimization problems. A new phase with high concentration of phosphorus element, namely boron pentaphosphide (BP₅), is obtained, which has a lower formation energy than that of commonly believed g-BP phase [21, 22, 25–27]. The calculations present that BP₅ monolayer is an unprecedented 2D material with five primary properties simultaneously, i.e. ferroelasticity, ferroelectricity, negative Poisson’s ratio, strongly anisotropic visible-light absorption and semiconducting property with high carrier mobility. More importantly, the AlN (0 1 0) surface is predicted to be a potential substrate for epitaxy growth of BP₅ monolayer, making BP₅ monolayer a candidate material for designing nonvolatile memory devices.

2. Computational methods

The structure search is employed by global optimization Cuttlefish algorithm [24] (see supplementary information (stacks.iop.org/TDM/4/045020/mmedia)) for different stoichiometric BₙPₘ (m ≤ 5 and n ≤ 5) compounds. Furthermore, we have reconfirmed the obtained structures with global minimum formation energy based on particle swarm optimization, as implemented in CALYPSO code [28]. All the first-principles calculations are performed on the basis of the Kohn–Sham density functional theory [29] (KS-DFT) as implemented in the Vienna ab initio simulation package [30] (VASP). The generalized gradient approximation as parameterized by Perdew, Burke and Ernzerhof [31] (PBE) for exchange-correlation functional is used to relax the geometric structures and the plane wave basis sets with kinetic energy cutoff of 450 eV are used to expand the valence electron wave functions. The convergence criterion for the energy in electronic SCF iterations and the force in ionic step iterations are set to be 1.0 × 10⁻⁶ eV and 5.0 × 10⁻³ eV Å⁻¹, respectively. A large vacuum space of at least 15 Å is introduced to prevent interlayer interactions between periodic images. The reciprocal space is sampled with a k-grid density of 9 × 12 × 1 using the Monkhorst–Pack scheme. Ferroelectric spontaneous polarization is calculated by using the Berry phase approaches [32, 33]. Besides, quasiparticle band structure is also calculated by many-body perturbation theory calculations with the G₀W₀ approximation [34, 35] and optical properties are obtained by solving two-particle Bethe–Salpeter equation (BSE) [36, 37]. Van der Waals (vdW) correction proposed by Grimme (DFT-D2) is used due to its good description of long-range vdW interactions for multi-layered 2D materials [38–42]. The mechanical properties of materials, such as elastic constants, Young’s modulus and Poisson’s ratio [43–45] are calculated by our PyGEC package [9] with VASP interface.

3. Structure and stability

We carry out variable components global optimization searching for different stoichiometric ratio compounds by repeated for each possible composition BₙPₘ (m ≤ 5 and n ≤ 5). Then the phase stabilities of different B–P system are evaluated firstly by judging the formation energy of BₙPₘ. If the formation energy of a compound is negative, this compound is considered to be stable with respect to decomposition into the elements. Clearly, the formation energy of BₙPₘ per atom is written as [46]:

\[
\Delta E(B_{m}P_{n}) = \frac{E(B_{m}P_{n}) - m\mu_B - n\mu_P}{m + n}
\]

where \(\Delta E(B_{m}P_{n})\) is the formation energy per atom; \(E(B_{m}P_{n})\) is the total energy of \(B_{m}P_{n}\) calculated by DFT. The chemical potential of B and P (\(\mu_B\) and \(\mu_P\)) are taken from the cohesive energy of α-B [47] and black phosphorene [48, 49], respectively. To account for all thermally stable structures, we construct the ‘convex hull’ or ‘global stability line’ of all considered binary phases [50]. As shown in figure 1(a), the formation energy \(\Delta E(B_{m}P_{n})\) is plotted as a function of molar fraction of boron element, and all points on the convex hull (solid line) are stable against all decomposition reactions. It can be found that most of the B–P compounds have positive formation energy (above the dashed line), however, the g-BP, BP₅ and two metastable phases of BP₅ (see supplementary information) have the negative ones. Here, we mainly focus on newly predicted BP₅ phase (figure 1(b)). Similar to black phosphorene, BP₅ has a puckered sheet of linked atoms with a puckered thickness \(d = 3.840 \) Å. The space group is Pm2m. The optimized lattice parameters are \(a = 4.635 \) Å and \(b = 3.278 \) Å. From top view, it can be found that BP₅ is composed of six-membered rings with boron and phosphorus atoms. The side view shows that BP₅ has a sandwich structure with a B–P single layer encapsulated by phosphorus atoms. It is worthy of noting that the formation energy of BP₅ is about \(-0.059 \) eV/atom, which is comparable or even lower than that value of g-BP \((-0.038 \) eV/atom), implying that BP₅ is also a potential stable phase of B–P compounds. It’s also deserved to note that the phosphorus concentration is much higher than that of boron during synthesizing boron–phosphorus compound [18], which is beneficial for producing BP₅.

As discussed above, a new phase BP₅ is proposed by global search algorithm. To further check the dynamical stability, the phonon band structure is calculated. The absence of imaginary mode in the whole 2D reciprocal space indicates that this monolayer is dynamically stable figure 1(c). Then ab initio molecular
AIMD simulations are carried out with a $5 \times 7$ supercell to verify the thermal stability of BP under finite temperature. After heating at 300 K for 5 ps (figure S4) with a time step of 1 fs, the structure does not suffer significant distortion or transformation, so does it at 400 K. In addition, the calculated elastic constants meet the necessary mechanical equilibrium conditions [51] for mechanical stability: $C_{11} - C_{12} > 0$ and $C_{11}, C_{22}, C_{66} > 0$ (see supplementary information). Therefore, all these analysis above demonstrates that BP is not only dynamically stable but also thermodynamically and mechanically stable.

4. Ferroelasticity and ferroelectricity

Since BP is predicted as a potential stable phase of low dimensional B–P binary compound, a further study of its intrinsic properties is desired. Firstly, we pay our attention to the ferroelastic switching of BP. A ferroelastic material is defined by the existence of two more equally stable orientation variants, which can be switched from one variant to another without diffusion by the application of external stress [52, 53]. The two orientation variants I and II of BP are shown in figures 2(a) and (b). As for the initial variant (I), the zigzag rows lie in $y$ direction, and the lattice constants $|b|$ along zigzag direction is shorter than that along armchair direction ($|a|$). If an external tensile stress is applied along the zigzag direction, it may transform into the variant II that will be energetically more favorable, where $|a'| = |b|$, $|b'| = |a|$ and zigzag rows are switched to the $x$ direction, same as the initial variant I upon $90^\circ$ rotation. The inverse rotation can also be realized if the external tensile stress is applied along the zigzag direction for variant II. To estimate the transformation process between variant I and II, the pathway for the mechanical transformation is computed by solid-state nudged elastic band (ss-NEB) method [54]. As shown in figure 2(b), the pathway for the mechanical transformation is computed by solid-state nudged elastic band (ss-NEB) method [54]. As shown in figure 2(b), the pathway for the mechanical transformation is computed by solid-state nudged elastic band (ss-NEB) method [54]. As shown in figure 2(b), the pathway for the mechanical transformation is computed by solid-state nudged elastic band (ss-NEB) method [54]. As shown in figure 2(b), the pathway for the mechanical transformation is computed by solid-state nudged elastic band (ss-NEB) method [54]. As shown in figure 2(b), the pathway for the mechanical transformation is computed by solid-state nudged elastic band (ss-NEB) method [54]. As shown in figure 2(b), the pathway for the mechanical transformation is computed by solid-state nudged elastic band (ss-NEB) method [54].
of switching. Compared with previously proposed ferroelastic materials \cite{8}, BP$_5$ displays a reversible ferroelastic strain up to 41.4\%, which is the highest value known to date.

Unlike black phosphorene, BP$_5$ monolayer is noncentrosymmetric and the electronegativity of phosphorus atom (2.19) is larger than that of boron atom (2.04). As a result, a spontaneous polarization occurs in BP$_5$ monolayer with the direction of polarization along the $+x$ direction in state I (figure 2(a)). The estimated intensity of polarization is $1.63 \times 10^{-10}$ C m$^{-1}$, which is comparable to that value of SnS ($2.47 \times 10^{-10}$ C m$^{-1}$) and SnSe ($1.87 \times 10^{-10}$ C m$^{-1}$) \cite{8}. Therefore, this phase is intrinsic ferroelectric as long as the polarization is switchable. When an external field is applied along the $-x$ direction for state I, the boron atoms with positive charge will move left and phosphorus atoms with negative charge will move right. Finally, the state III will be obtained with the direction of polarization along the $-x$ direction. The pathway of ferroelectric switching between ferroelectric state I and III is shown in figure 2(c). The corresponding upper limit of switching barrier can be estimated by using the NEB method, for which the state Tr2 with a square lattice can be viewed as the intermediate state with a switching barrier about 0.41 eV/atom. Furthermore, if an external field is applied along the $-y$ direction for state II, all atoms will move similarly and transform into state IV, which has a direction of polarization along the $-y$ direction, the polarization is switched. Because of the symmetry, the reaction path from state II to state IV should be identical, and follows the same path as the ferroelectric switching shown in figure 2(c). As we discuss above, the state I and II can be associated with external stress, however, we can also realize this switch by applying external field to state I along $+y$ direction, with the same pathway and switching barrier as in figure 2(b). Therefore, BP$_5$ monolayer is an intrinsic multiferroic material with coupled ferroelectricity and ferroelasticity, suggesting it has potential applications in memory devices.

5. Negative Poisson’s ratio

Our previous work \cite{9} has demonstrated that hingelike structures, such as SnSe \cite{55}, black phosphorene \cite{11} and BP have the auxetic effect \cite{10, 11, 56, 57}. Due to the similar geometric structure, it is expected that auxetic effect may also exist in BP$_5$. Figure 3 shows that BP$_5$ indeed expands along out-of-plane direction when an external tensile stress is applied in zigzag direction. This indicates that BP$_5$ also holds a fascinating auxetic effect. Further calculation estimates that the negative linear Poisson’s ratio is $\nu = -0.037$ along the out-of-plane direction, which is a little higher than that of black phosphorene ($\nu = -0.027$). Recently, an experimental work \cite{58} has successfully demonstrated the negative Poisson’s ratio of black phosphorene, thus it is expected that auxetic effect of BP$_5$ could be validated by experiment in future.

6. Electronic structure and optical properties

The ferroelasticity and ferroelectricity of BP$_5$ discussed above will have more profound impact if they are also coupled to electronic and optical properties. The band structure and density of states (DOS) calculated under GGA-PBE level (see supplementary information figure S6) indicate BP$_5$ to be a semiconductor with an indirect band gap of 0.328 eV. The valence band maximum (VBM) is at $\Gamma$ point and the conduction band minimum (CBM) is located between Y and $\Gamma$ points. The decomposed DOS demonstrates that the VBM is a hybrid-state of phosphorus and boron atoms, while the CBM is mainly contributed by phosphorus atoms. Since the GGA-PBE functional significantly underestimates band gaps, the quasiparticle effect is then involved based on many-body perturbation theory within the G$_0$W$_0$ approximation to obtain the accurate band gap \cite{34, 35}. As shown in figure 4(a), the indirect band gap of BP$_5$ is increased to 1.34 eV and the corresponding direct band gap is 2.53 eV. At the same time, the photoabsorption spectrum is also calculated by solving the Coulomb BSE \cite{36, 37} based on the quasiparticle energies and the screened Coulomb interactions obtained from the GW calculations. Figure 4(b) displays the calculated imaginary dielectric functions including the excitonic effect. BP$_5$ monolayer presents a highly anisotropic photoabsorption with two giant low-energy excitonic peaks: one at 1.60 eV for $yy$ component and the other at 1.85 eV for the $xx$ component of the dielectric tensor. Noting their corresponding direct quasiparticle transition energy is 2.54 eV and 2.62 eV respectively, we evaluate large exciton binding energies of 0.94 eV and 0.77 eV. These excitonic behaviors and strongly anisotropic absorption are similar to other 2D materials \cite{59}.

The inherent orthorhombic waved structure of BP$_5$ also results in the orientation-dependent effec-
tive carrier masses. As summarized in table 1, hole has a large effective mass of 3.586 \( m_0 \) and electron has a small value of 0.346 \( m_0 \) along the zigzag direction. However the effective masses of electron and hole along the armchair direction have relatively small values, which are comparable to the values of phosphorene (0.17 \( m_0 \) and 0.15 \( m_0 \)) [60, 61]. Carrier mobility is known to be a crucial factor for electronic and optoelectronic applications because high mobility can prevent electrons and holes from recombination [62] and have promising applications to future high-performance electronic devices [63]. Therefore, we calculate the carrier mobility based on the deformation potential (DP) theory as proposed by Bardeen and Shockley (see supplementary information) [64]. The calculated carrier mobility is orientation-dependent as one would expect from the anisotropic nature of the calculated effective masses and mechanical properties. For example, the mobility of electrons along the zigzag direction is higher than that of armchair direction. The underlying reason is that the DP for electrons along the zigzag direction is relatively small as compared to armchair direction. Apart from the anisotropic electronic conductance, BP\(_5\) also presents a large value of the carrier mobility. Especially, the carrier mobility at room temperature is up to 7.06 \( \times 10^3 \) \( \text{cm}^2 \text{V}^{-1} \text{s}^{-1} \), which is comparable or even higher than that value of black phosphorene (DFT: 2.20 \( \times 10^3 \) \( \text{cm}^2 \text{V}^{-1} \text{s}^{-1} \) [65]; Experiment: 1.0 \( \times 10^3 \) \( \text{cm}^2 \text{V}^{-1} \text{s}^{-1} \) [66]), and significantly larger than other 2D materials, such as MoS\(_2\) (DFT: 320 \( \text{cm}^2 \text{V}^{-1} \text{s}^{-1} \) [67]; Experiment: 200 \( \text{cm}^2 \text{V}^{-1} \text{s}^{-1} \) [68]), making BP\(_5\) very promising for application in electronic devices.

### 7. Possible epitaxy substrate

Although 2D BP\(_5\) shows intriguing electro-mechanical properties for potential applications to electronic devices, how to synthesize this material is still a critical issue. Therefore, we turn to investigate possible substrate for synthesizing BP\(_5\) monolayer. AlN is reported to be an excellent substrate for growth of cubic boron phosphide. However, unlike the experimental one [20] where AlN (0 0 1) surface is used and cubic boron phosphide [1 1 1] orientation is predominant, we here find AlN (0 1 0) surface is a suitable substrate for epitaxy growth of BP\(_5\). The optimized atomic configuration of AlN (0 1 0) surface with adsorbed BP\(_5\) (marked as BP\(_5\)@AlN(0 1 0)) is shown in figure S7. In addition, ab initio molecular dynamics (AIMD) simulations are also carried out with a 2 \( \times \) 3 supercell to verify the thermal stability of BP\(_5\)@AlN(0 1 0) under finite temperature. After heating at 300 K for 5 ps (figure S8) with a time step of 1 fs, it can be found that BP\(_5\) can sustain on the AlN substrate without notable distortion. Therefore, AlN (0 1 0) surface will be a potential substrate for synthesizing BP\(_5\) monolayer. To guide future experiments, we also provide the STM image for BP\(_5\)@AlN(0 1 0) (see figure S7).

### 8. Conclusions

In summary, based on global optimization Cuttlefish algorithm, a new fascinating 2D material composed of boron and phosphorus element, namely BP\(_5\), is proposed. We find that BP\(_5\) is a multiferroic material with coupled ferroelectricity and ferroelasticity.
Particularly, BP₅ possesses the highest reversible ferroelastic strain known till now and a ferroelectric polarization which is absent for black phosphorene. Moreover, BP₅ is an indirect semiconductor with a band gap of 1.34 eV and displays outstanding mechanical, optical and electronic properties, such as negative Poisson’s ratio, strongly anisotropic visible-light absorption and high carrier mobility. Finally, AlN (0 1 0) surface has been demonstrated to be a potential substrate for epitaxy growth of BP₅ monolayer.

Due to the fascinating properties of BP₅, a potential application to electronic devices, particularly memory devices [8, 59], is proposed here. Taking ferroelectric memory as an example, the initial states of spontaneous polarization direction is shown in the left panel of figure S9, which can be labeled as information ‘000’. By applying large electric field, one can switch the polarization direction and then the information ‘100’ will be saved into the device, which is stored in a permanently accessible, nonvolatile form as the polarization will be saved into the device, which is stored in a permanently accessible, nonvolatile form as the polarization state cannot be changed spontaneously. Considering its strongly anisotropic visible-light absorption and highly anisotropic carrier mobility of BP₅, the ‘reading’ process can be realized by either of three methods: (1) measuring current–voltage curve under small bias; (2) detecting photocurrent upon photo-illumination since the internal electric field will determine the drifting direction of photoexcited charge carriers; (3) measuring polarization-dependent photoluminescence. For ferroelastic memory, ‘writing’ process can be realized by external tensile stress and ‘reading’ by a similar way as in ferroelectric memory. We hope our research can stimulate future experiments on this subject.

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