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Stability and electronic structure of two-dimensional arsenic phosphide monolayer

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ABSTRACT

Using first-principles calculations, we investigate the geometric structures, stabilities, electronic structures, and magnetic properties of three kinds of AsP monolayers: blue-phosphorene-like AsP (blue AsP), black-phosphorene-like AsP (black AsP) and puckered AsP. Stability analysis implies a high possibility of fabricating AsP monolayers in experiments. The blue AsP monolayer possesses the most stable structure with an indirect band-gap of 2.52 eV. The blue AsP system is also a good candidate for visible light photocatalytic decomposition of water. The black one is a semiconductor with a direct band gap of 1.53 eV at the Γ point. The puckered AsP monolayer shows the lowest stability and narrowest indirect band gap of 1.38 eV. Both the intrinsic defects of P and As vacancies result in half-metallicity and magnetic semiconductor for blue and black AsP monolayers, respectively. Our results provide useful information to obtain new two dimensional materials for water splitting photocatalysts and spintronic devices.

1. Introduction

Recently, a surge of interest has been poured into research of two dimensional (2D) materials, such as graphene [1], hexagonal boron nitride [2], and transition metal dichalcogenides [3], due to their unique physical properties and potential applications in nanoelectronics [4–6]. The synthesis of graphene encourages people to hotly search for new 2D materials of other elements in diverse structures. Phosphorene, a monolayer of black phosphorus, was recently synthesized by mechanically exfoliating black phosphorus [7]. In addition, Zhang et al. reported that they prepared large-scale and high quality atomic-layered blue phosphorus on Au(111) by molecular beam epitaxy [8]. The two kinds of phosphorus monolayes are referred to as black and blue phosphorene, respectively, named after their layered bulk materials [9].

Besides phosphorene, theoretical studies have suggested many other postulated structures, such as nitrogene [10], arsenene [11,12], antimonene [13], and bismuthene [14,15], that could be stable or synthesized. These studies have inspired research interest in V-V compounds [16–18]. However, much more interest was focused on the black-phosphorene-like and blue-phosphorene-like structures of group-V binary compounds. The V-V compounds should possess fairly rich geometric structures, and physical and chemical properties. However, the theoretical predictions do not have complete agreement on some properties of V-V compounds [16–18]. The detailed and systematic information are still unreliable for AsP compound. Moreover, experiments had affirmed the existence of AsP system [19–22]. Adopting the alloying strategy, Liu et al. synthesized a family of black arsenic–phosphorus (b-As$_x$P$_{1-x}$) [21]. The stability and synthetic route of the family of b-As$_x$P$_{1-x}$ has also been examined by Osters et al. [22]. Nonetheless, the 2D honeycomb-like AsP has not yet been explored systematically for their structural stability, or their electronic and optoelectronic properties. Therefore, it is necessary to gain further insights into the physical properties of AsP monolayer.

Based on density functional theory (DFT), we investigate the geometric structures, energetic stability, thermodynamic and mechanical stability, as well electronic structures and magnetic properties of three kinds of AsP monolayers. They are blue-phosphorene-like AsP (blue AsP), black-phosphorene-like AsP (black AsP), and δ-phosphorene-like AsP (puckered AsP). It is also worthwhile note that As$_x$P$_{1-x}$ materials possess good tunability of the chemical compositions, which leads to tunable band gaps and optical properties in AsP materials. In this work, we only consider the AsP systems with ordered distribution and equal amounts of As and P. Additionally we examine the effect of intrinsic defects of P vacancy (P$_V$) and As vacancy (As$_V$) on electronic structure and magnetic properties of AsP monolayers. The blue monolayer is

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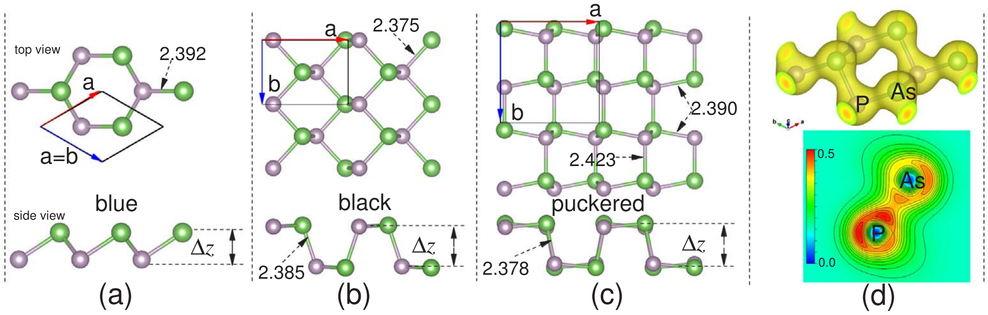

Fig. 1. Top and side views of the optimized (a) blue, (b) black, and (c) puckered AsP structures. (d) The charge density isosurfaces of blue AsP, and the contour plot of charge density in plane passing through P and As atoms. The prism or rectangle indicates a unit cell. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Table 1
Structural parameters, relative stability energy (ΔE) and formation energy (E_f), band gap calculated with PBE and HSE06 functionals, charge transfer from As to P ($\Delta\rho$), and linear elastic constants.

Type	Lattice	ΔZ (Å)	ΔE (eV)	E_f (eV)	Band gap (eV)		Δρ	Elastic constants (N/m)			
	a/b (Å)				PBE	HSE06		C_{11}	C_{12}	C_{22}	C_{66}
Puckered	5.591/5.721	2.50	0.1304	0.224	0.79	1.38	0.238	36.6	−12.1	59	9.7
Black	3.497/4.703	2.34	0.0386	0.143	0.90	1.53	0.237	18.9	18.2	79.8	19.5
Blue	2.993	1.32	0.0	0.094	1.82	2.52	0.184	63.4	9.6		

found to be the most stable structure with indirect *band gap* of 2.52 eV which makes it suitable for photocatalysts for water splitting in visible light. The black one is a semiconductor with a direct band gap of 1.53 eV at the Γ point. The puckered monolayer is a promising auxetic material.

2. Computational details

To simulate 2D AsP structures, three kinds of structures are considered based on the clues to structural information on PN [17] and As_xP_{1-x} systems [16,18,21,22]. For the sake of discussion, they are named as blue, black, and puckered AsP monolayers, as shown in Fig. 1. We carry out first-principles calculations using density functional theory (DFT) in the generalized gradient approximation (GGA) [23] of Perdew-Burke-Ernzernh (PBE) [24] method for the exchange-correlation function as performed in the Vienna *ab initio* Simulation Package code (VASP) [25]. The projector augmented wave (PAW) method [26] is used for the description of the electron–ion interactions. A kinetic energy cutoff of 460 eV is employed in a plane-wave basis set. For geometry optimization, the atomic positions are fully relaxed until the Hellmann–Feynman forces on each atom are smaller than 0.01 eV/Å. A vacuum space of 14 Å normal to the plane of the 2D systems is adapted to eliminate the interaction between neighboring images. To obtain density of state (DOS), the Brillouin zone (BZ) is sampled with 13 × 13 × 1 Γ-centered Monkhorst-Pack [27] grids for blue AsP, and with 8 × 12 × 3 Monkhorst–Pack *k*-points for black or puckered AsP structure.

To assess the energetic stability of the three structures, formation energy is obtained by using the expression:

$$E_f = (E_{total} - n\mu_P - n\mu_{As})/n \tag{1}$$

Here, the E_{total} denotes the total energy of a AsP unit cell, μ_P and μ_{As} represent the chemical potentials of P and As elements, respectively. The n is the number of P or As atoms in a unit cell. Here μ_P is the energy of a P atom in bulk black phosphorus (α-P), and μ_{As} is the energy of a As atom in bulk gray arsenic (β-As). To evaluate the dynamic stability, the phonon spectrum calculations are implemented in the Phonopy [28] within the framework of finite displacement method. To verify the thermal stability of the AsP monolayers, we perform molecular dynamics (MD) simulations which are carried out at 750 K with a time step of 1 fs for 6 ps. Temperature control is achieved by the Nosé thermostat model [29]. Due to the self-interaction error in the PBE functional, the large underestimation of the band gap is a well-known problem in standard DFT calculations. For this reason, we also carry out calculations using the hybrid functional (HSE06) [30] with standard mixing 25% of the Fock exchange and with 75% of the PBE exchange. Due to time-consuming calculations, HSE06 only is used to obtain band structure.

3. Results and discussions

To begin with, we consider the structures and stabilities of AsP monolayers. The optimized blue, black and puckered structures belong to *P*3*m*1, *Pmn*21 and *Pca*21 space groups, respectively, as shown in Fig. 1. The side view of the puckered structure shows a ridge-like configuration that is, to some extent, analogous to that of δ-phosphorene [17]. All the three monolayers show buckled structures with buckling height Δz is 1.32 Å, 2.34 Å and 2.50 Å, respectively. The structural parameters of the three AsP structures are listed in Table 1. Lattice vectors of $\vec{a}$ and $\vec{b}$ direct along armchair and zigzag direction, respectively, for both the black ($\vec{a}$ = 3.497 Å, $\vec{b}$ = 4.703 Å) and puckered ($\vec{a}$ = 5.591 Å, $\vec{b}$ = 5.721 Å) structures. The blue AsP monolayer is a buckled honeycomb lattice $\vec{a}\vec{b}$ = 2.993 Å, and the bond angle is obtained as 92.495°. The bond lengths of the blue (2.392 Å), black (2.375, and 2.385 Å), and puckered (2.378, 2.390, 2.423 Å) structures are labeled in Fig. 1.

To assess the stability of the monolayer compounds, we firstly examine the relative stability by calculating the relative stability energy based on the expression $\Delta E = E - E(\text{blue})$, *i.e.*, the energy difference relative to blue AsP monolayer. The results (energy per formula unit) in Table 1 show that the blue AsP monolayer is the most stable in energy, while the puckered case has the highest energy. Besides the three structures, we also consider planar AsP monolayer and find its total energy is higher than that of blue case by 1.261 eV per formula unit. Similarly, the E_f is calculated to evaluate their thermodynamic stabilities. The slight E_f of 94 meV per formula unit implies that it is easy to prepare blue monolayer from its constituents at their stable bulk structures, since the α- and β-P, As, Sb, and bi-layered bulk crystals were found to experimentally exist [31]. The E_f is a function of the chemical potentials. The formation energies will become smaller by assuming the chemical potentials at their respective upper limits, *i.e.*, at their atomic energies [18].