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# Point defects in buckled and asymmetric washboard phases of arsenic phosphorus: A first principles study

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ABSTRACT

Based on first-principles plane wave method within density functional theory using the generalized gradient approximation, we investigate the effects of point defects on the electronic and magnetic properties of single-layer phases of AsP. We predict that these properties of buckled and asymmetric washboard structures of AsP can be modified by various kind of point defects including single and divacancy, antisite and substitutions. While single-layer buckled AsP structure displays semiconducting properties, it becomes either metal or narrow band gap semiconductor in the presence of point defects. On the other hand, the nonmagnetic direct-gap semiconductor asymmetric washboard AsP is found to be metallic upon defect creation. All the creation of point defects have zero net magnetic moment, except asymmetric washboard phase of AsP with P vacancy. We calculated $\mu = 1.19\ \mu_B$ for relaxed structure of the P-single vacancy. Our results show that free-standing single-layer phases of AsP functionalized by point defects can serve as interconnects between AsP based spintronic devices.



## 1. Introduction

Two-dimensional (2D) single-layer (SL) honeycomb structures have exceptional properties and thus attracted a growing interest with their promising applications in nanotechnology. Recent studies in nanoscale physics have enable the discovery of new single-layer materials with a wide range physical and chemical properties under different conditions. The search for the contender of graphene [1,2] has led to the prediction/synthesis of new single-layer, crystalline nanostructures, which do not exit in nature. Silicene, germanene, stanene, namely graphene analogs of group IV or V elements [3–8]; h-BN analogs of group IV-IV, III-V, and II-VI compounds [9–13]; graphyne [14–16] and the auxetic piezoelectric 2D material silicatene with negative Poissons ratio [17,18] have been actively studied. Additionally, transition-metal dichalcogenides have proven to be superior than graphene in specific optoelectronic applications [19–23]. However, practical application of these materials are likely limited due to either the zero-band gap in group IV elements or the relatively low mobility in transition-metal dichalcogenides. In the long term, the development of new semiconductor with a desired properties will become important. Therefore, having particular band gap and high carrier mobility of semiconductor have been of particular interest.

Recently, the synthesis of 2D single-layer structures of black phosphorus was achieved by exfoliating a few layers from its bulk counterparts. Following the synthesis of few layers phospherene, single-layer structures of group-V element such as Nitrogene [24], Phosphorene [25–28], Arsenene [29–31], Antimonene [32] and Bismuthene [33] have been found as stable [25,29,32,33] and the mechanical and electronic [33,34] properties were investigated. Because of their direct or indirect band gap properties, these single-layer structures can be promising materials for digital circuits and light-emitting diodes. Furthermore, few-layer and/or single-layer structures of group V elements, including phosphorene and arsenene, are emerging as promising candidates for two-dimensional (2D) electronic materials application [35–39]. Recently, the fabrication of field effect transistors using micrometer-sized flakes consisting of two and three layers of black phosphorus [40] and their theoretical analysis [25,41] revealing the stability of its single-layer allotropes brought group V elements into the focus.

Different from single-layer of group-IV elements, these materials display a nonzero band gap while still maintaining a relatively high carrier mobility [42–45]. Although a wide range in electromagnetic spectrum has been covered by these 2D SL materials,

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there is still a big need to different smart materials because of the light radars and atmosferic applications in the long wavelength spectrum range. On the other hand, because of its direct band gap, black phosphorus is currently considered the best material on-chip detectors. Besides all of these advantages, few-layer black phosphorus samples have displayed high reactivity. On the other hand, layered gray arsenic changes this disadvantage into advantage with its the unique properties. Therefore, arsenene is also begin to attract attention with high mobility and excellent contact with electrode materials. In order that reason, the combination of black phosphorus and gray arsenic may exhibit phase coexistence that should bring an unexpected richness in both structural and electronical properties, in comparison to pristine of phosphorene and arsenene, has already been shown by the end of year 2015 and early 2016 [46–51]. These are buckled honeycomb (*b*-AsP) or hexagonal and asymmetric washboard structures (*aw*-AsP). Very recently, the *aw*-AsP was indeed synthesized adopting alloying strategy [39]. Although both buckled and asymmetric washboard single-layer arsenene are stable structures which are shown by phonon spectrum and with theirs cohesive energies, they possess indirect band gaps of 0.831 eV and 1.635 eV, respectively [29–31]. Beside Si, Ge, and Sn single-layers and with the development of experimental technology, SL-AsP has the advantage of manufacturing by exfoliating crystalline black phosphorus which has been shown recently by Liu et al. [39]. Therefore AsP is chosen as the research objective of interest here. We believe that SL *b*-AsP will also be realized like its counterpart *aw*-AsP and the numerous other single-layer structures which were realized in the laboratory after the prediction of them with first principles calculations. As a matter of fact, serious experimental attempts have started to produce very thin sheets of these monolayer where *aw*-AsP has been recently synthesized [39]. Interestingly, silicene, antimonene and many other phases have been synthesized generally after ab initio calculations [32]. Previous experimental and theoretical studies have proven that bare 2D single-layer structures can be functionalized through point defects to attain crucial physical and chemical properties for diverse applications [52–56].

In this manuscript, motivating by recent studies of phases of phosphorene and arsenene, our aim is modifying the indirect gap of arsenene by making black arsenic phosphorus or in other words by substitution of arsenic atoms to phosphorene. Here, we deal with the effects of the point defects on the physical properties of *b*-AsP and *aw*-AsP. We found that the point defects modify the electronic and magnetic properties. In this respect, while nonmagnetic and semiconducting *b*-AsP can be metallized by As and P vacancies, it remain semiconductor upon either periodic As+P divacancy and antisite, As-P or P-As substitution defects. While the *aw*-AsP, which is a semiconductor, is found to be nonmagnetic and metallic as a result of vacancy defects of As vacancy, As+P divacancy, antisite and substitution, the creation of P-single vacancy gives rise to a net magnetic moment of $\mu = 1.19\ \mu_B$ per unit cell.

## 2. Calculation methods

Our results are obtained from first-principles plane-wave calculations based on spin-polarized density functional theory (DFT) using projector augmented wave (PAW) potentials [57]. The exchange-correlation potential is approximated by generalized gradient approximation (GGA) using Perdew-Burke-Ernzerhof (PBE) parametrization [58]. All numerical results have been obtained by using Quantum Espresso software [59]. A plane-wave basis set with the kinetic energy cutoff $\hbar^2(k+G)^2/2m =$ 884 eV is used. Pseudopotentials with $4s^2 3d^{10} 4p^3$ and $3s^2 3p^3$ valence electron configurations for As and P atoms were used, respectively. All structures are treated using periodic boundary conditions.

The Brillouin zone has been sampled by $(21 \times 21 \times 1)$ and $(7 \times 7 \times 1)$ special mesh points in k-space by using Monkhorst-Pack scheme [60] for $(1 \times 1)$ and $(4 \times 4)$ AsP cells, respectively. All atomic positions and lattice constants are optimized by using BFGS quasi-Newton algorithm [61] where the total energy and forces are minimized. The convergence criteria for energy is chosen as $10^{-6}$ eV between two consecutive steps. The maximum Hellmann-Feynman forces acting on each atom is less than 0.01 eV/Å upon ionic relaxation. The maximum pressure on the unit cell is less than 0.5 kbar. Gaussian type Fermi-level smearing method is used with a smearing width of 0.1 eV. All charge density

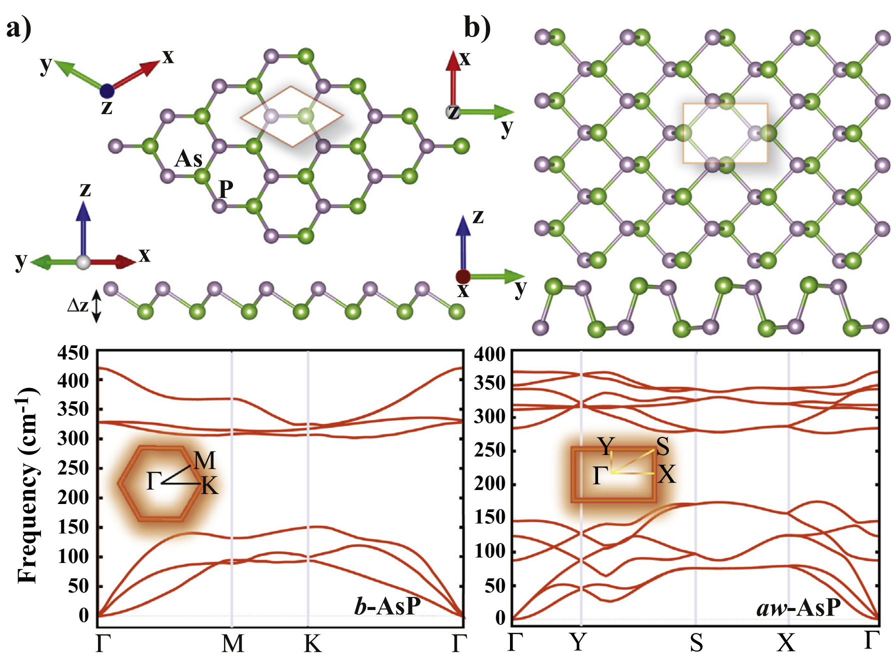


**Fig. 1.** (a) Side and top views of the optimized atomic configuration of the $(1 \times 1)$ primitive unit cell of *b*-AsP and calculated phonon frequencies versus k of *b*-AsP. (b) Same for the bare *aw*-AsP.