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Electronic and magnetic properties of Ga, Ge, P and Sb doped monolayer arsenene

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ABSTRACT

In this paper, the structural, electronic, and magnetic properties of Ga, Ge, P and Sb doped monolayer arsenene have been systematically investigated by first-principles calculations based on density functional theory. The properties of monolayer arsenene can be effectively tuned by substitutional doping. Especially, the dopant Ga could lead to an indirect-to-direct bandgap transition and doping a Ge atom could exhibit dilute magnetic semiconductor property. In addition, the second Ge atom slightly prefers to occupy the next nearest-neighbor site of As atom to form the complex substituted defect (Ge_{As} - As - Ge_{As}) in $As_{30}Ge_2$ system and is found to be anti-ferromagnetic coupling. The diverse electronic and magnetic properties highlight the potential applications of monolayer arsenene in electronics, optoelectronics and spintronics.

1. Introduction

Two-dimensional (2D) layered materials have witnessed a surge in research interest since the discovery of graphene due to their unique properties and potential applications in nanoelectronics and spintronics [1–4]. The impressive progress in graphene research has motivated scientists to explore other 2D atomic based materials [5].

Few-layer structures of group V elements, including phosphorene and arsenene, are emerging as promising candidates for 2D electronic materials application [6–10]. Interestingly, it has been predicted to adopt buckled structures to increase the kinetical stability and the electronic structure of arsenene can be effectively modified by strain using *ab initio* density functional calculations [11–13]. A detailed investigation on the electronic structure and carrier mobility of arsenene nanosheet and nanoribbon [14,15]. Kamal *et al.* systematically studied the buckled and puckered monolayer arsenene exhibit an indirect-to-direct gap transition in response to the uniaxial strain effects or an external electric field [11]. Zhang *et al.* further revealed that among several possible allotropes with typical honeycomb and non-honeycomb structures of monolayer arsenene, β-arsenene has the best stability and possesses carrier mobility as high as several thousand $cm^2V^{-1}s^{-1}$ [16]. In addition, free-standing monolayer arsenene is indirect band-gap and should be grown easily to form quasi-2D structures due to the similar cohesive energies between the buckled structure and bulk arsenic [11].

Nevertheless, some important issues remain unexplored, for example, how to effectively tailor the electronics and magnetic properties of monolayer arsenene to enlarge the application of optical and spintronics devices. Recently, functionalization on 2D films is one of a very important way to tailor the fascinating electronic properties, like as to realize the semimetal-semiconducting and Dirac materials, and so on [17–20]. Monolayer arsenene is nonmagnetic, which is similar to most of pristine 2D materials [4–6]. The hydrogenated arsenene can act as planar magnet and Dirac material, and the halogenated arsenene films can act as quantum spin Hall insulator [21–24]. Recently, the fascinating electronic and magnetic properties of the substitutional doping in some 2D materials, such as graphene, BN sheets and MoS_2 monolayer, have experimentally achieved by filling the vacancies created by the electron beam with substitutional atoms [25–27]. Yan et al. have reported that a doping C, Si, O and S atom and a vacancy induce the magnetism in buckled arsenene [28]. Moreover, defects and substitutional doping can also induce that 2D materials possess the magnetism and show unexpected electronic properties [29–33]. Sun et al. have reported that the electronic and magnetic properties are tuned by substituted doping in germanane [34,35], blue phosphorene [36] systems. In addition, the structural, electronic, and magnetic properties of arsenene monolayer atoms have reported by substituted and adsorbed doping [37,38]. Therefore, these findings motivate us to investigate the unrevealed electronic and magnetic properties of arsenene by substitutional doping.

Therefore, in this paper, the structural, electronic and magnetic properties of Ga, Ge, P and Sb substitutional doped arsenene are

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extensively investigated based on first-principles calculations within density functional theory (DFT). Meanwhile, Band structure distribution (BS), the Density of States (DOS), atom Mulliken charges and the population analysis are performed to determine changes of atomic and electronic structures of doped arsenene. We aim to provide a theoretical foundation for the manufacture of novel 2D arsenic materials, which is essential to employ them as electronics, optoelectronics and spintronics nanodevices in the future.

2. Computational methods

The simulations are based on the spin-polarized density functional theory (DFT), which is provided by DMOL^3 [37–39]. The generalized gradient approximation (GGA) with the Perdew-Burke-Ernzerhof scheme (PBE) [40] is adopted for the exchange-correlation potential to optimize geometrical structures and calculate properties. Double numerical atomic orbital plus polarization (DNP) is chosen as the basis set, with the global orbital cutoff 4.4 Å. Similar functional have been successfully used to study the structural and electronic properties of GNRs, Si and Cu nanowires [41–43]. The vacuum space between monolayer arsenene is greater than 20 Å to ensure no interactions between different layers. Periodic boundary conditions are adopted for all utilized models in this work. The Brillouin Zone (BZ) is sampled by 6×6×1 (10×10×1) k-points for all structures in the geometry optimization (electronic) calculations [44], which brings out the convergence tolerance of energy of 1.0×10^{-5} Ha (1 Ha=27.2114 eV), maximum force of 0.002 Ha/Å, and maximum displacement of 0.005 Å. The electronic distributions of monolayer arsenene are carried out by Mulliken charge analysis, which is performed using a projection of a Linear Combination of Atomic Orbitals (LCAO) basis and to specify quantities such as atomic charge, bond population, charge transfer etc. LCAO supplies better information regarding the localization of the electrons in different atomic layers than a plane wave basis set does [45]. The obtained relative values of the charge e, but not the absolute magnitude, display a high degree of sensitivity to the atomic basis set and a relative distribution of charge [46,47].

3. Results and discussion

The accuracy of our calculation procedure is firstly tested by the structural, electronic and magnetic properties of pristine monolayer arsenene. The full relaxed lattice constant of monolayer arsenene is 3.55 Å, the As - As bond length is 2.492 Å, the bond angle is 91.778◦ and the buckle height h of two inequivalent As in two planes is 1.408 Å (see the side view of left panel of Fig. 1(a)), which agrees well with other theoretical results [11,16,27,32].

A 4×4×1 supercell of monolayer arsenene containing 32 atoms is constructed (Fig. 1a). Accordingly, the band structure of the supercell is shown in Fig. 1(b). The valence band maximum (VBM) appears at G point, and while the conduction band minimum (CBM) lies between the G and M points, which indicate that the monolayer arsenene is a semiconductor with an indirect band gap (E_g) of 1.746 eV. The calculated results also in good agreement with the previous theoretical band-gap value 1.635 eV [11]. In addition, Fig. 1(b) further shows that PDOS of monolayer arsenene that both s and p orbitals have contributions to the states near the Fermi level. However, the contributions from the p orbitals to the total DOS are much higher than that from s orbitals. The energy region near the Fermi level is dominated by the p orbitals of As atoms, which is a common feature of monolayer honeycomb systems such as silicene and blue phosphorene, where sp^3-like bonds form a nonplanar honeycomb structure. An indirect band gap in monolayer arsenene resembles that of buckled (blue) phosphorene [48]. Similar to blue phosphorene, each As atom in monolayer arsenene has three equivalent covalent bonds with its neighbors, which means that three electrons of As atom are saturated, while the other two electrons are a single lone pair. As a result, the five valence electrons of each As atom are all paired, and thus the pristine monolayer arsenene is intrinsically nonmagnetic [49].

As previously theoretical results mentioned, doping can tune 2D layered materials' chemical and physical properties [27–32,50–54]. Next we investigate the substitutional X-doped monolayer arsenene systems $As_{31}X$ (X = Ga, Ge, P and Sb), in which a substitutional X atom occupies a As site in the supercell. After the structure relaxation, for X-doped monolayer arsenene systems $As_{31}X$, the dopant atom at site 1 in Fig. 1(a) moves a little inside or outside of the plane, which is maintain the 3-fold symmetry. It can be deduced that all impurities form covalent bond with three nearest As atoms [35,36] and with equal values of bond lengths $l_{X1\text{-}As2}$, $l_{X1\text{-}As3}$, and $l_{X1\text{-}As4}$. Correspondingly, the calculated structural properties of doped gray arsenene are listed in Table 1. The bond lengths $l_{X1\text{-}As2}$ of impurity X with the nearest As atom are generally range from 2.394 to 2.674 Å. It can be seen that the Ga, Ge, and P -doped arsenene systems show a shrinkage in As-X bond length with respect to the original As-As bond (2.492 Å), while the Sb atom move outward from its initial substitution site and hence the As-Sb bonds become longer. Therefore, the height h of impurity atoms generally ranges from 0.398 to1.683 Å, varying with different impurity atoms.

Meanwhile, the stability of the substitutional systems is investigated by the binding energy. The binding energy (E_b), calculated as a difference between the energy of the substitutional system $As_{31}X$ and a monolayer arsenene with a single vacancy As_{31} plus energy of the isolated atom X, are presented in Table 1. The values of E_b are generally range from −4.458 to −5.391 eV, which is comparable with E_b of transition-metal (TM) atoms embedded in single vacancy in a graphene sheet and monolayer or bilayer black phosphorus [48–50,53]. These systems are rather stable and could be experimentally fabricated.

The atomic charge near the dopant of $As_{31}X$ system is analyzed by Mulliken analysis and the corresponding results are shown in Table 1. The Mulliken population of the Ga, Ge, P and Sb atoms are 0.651, 0.232, 0.204, and 0.240 e, respectively, which display that there are obvious electrons transfer between doping atoms and As nanosheet, indicating strong coupling between impurity atom and As atom. The electrons always transfer from the As atoms to the impurity atoms. This is because As atoms have a higher electronegativity than Ga, Ge, P and Sb atoms [51].

The electronic band structures of Ga, Ge, P and Sb doped monolayer arsenene are presented in Fig. 2(a)-(d). In order to deeply understand the contribution of different orbitals to the electronic states, total (DOS) and partial (PDOS) densities of states are also carried out to these structures, and the results are summarized in Fig. 3(a)-(d). The substituted systems could be divided into three categories.

The first category is Ga-doped monolayer arsenene, the doping of Ga impurity leads to an indirect - direct bandgap transition. The VBM and CBM all located at the G point in BZ in Fig. 2(a). The value of the band gap is approximately 1.348 eV. The spin-up and spin-down PDOS of Ga-doped monolayer arsenene are symmetric in Fig. 3(a), which indicate the non-magnetic ground states. The second category is Ge-doped monolayer arsenene, which has less valence electrons than As atom, create acceptor defect states above the valence band edge, thus resulting in p-type doping of arsenene in Fig. 2(b). In addition, Fig. 3(b) also shows that the spin-up and spin-down doping states of Ge-doped arsenene are not symmetric and distribute on the both sides of Fermi level, which indicates that Ge-doped arsenene system exhibit the magnetic ground states and has shown dilute magnetic semiconductor behaviors. The third category including P and Sb, the indirect band gap feature remains unchanged and the values of bandgap are calculated to be approximately 1.561 and 1.440 eV, respectively in Fig. 2(c) and (d). The spin-up and spin-down PDOS of P and Sb doped monolayer arsenene are symmetric in Fig. 3(c) and (d), which are also the non-magnetic semiconductors.