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The influence of dopants on aW-phase antimonene: theoretical investigations

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We systemically investigate the effect of dopants on the geometrics, electronic and magnetic properties of asymmetric washboard structure of antimonene (aW-Sb) by using density functional theory (DFT) calculations. The large binding energies and short bond lengths indicate the doped systems still maintain high stability. Pristine aW-Sb is a nonmagnetic semiconductor with a narrow band gap, while the doped aW-Sb exhibit metallic by doping. Furthermore, the Ti, V, Cr, Mn and Fe doping induced magnetic states, and the result of spin density indicates that the magnetic moments are mainly localized at dopant and the adjacent Sb atoms.

1. Introduction

Two-dimensional (2D) materials, such as graphene, transition metal dichalcogenides (TMDs), phosphorene, and silicene, have attracted considerable attention because of their intriguing mechanical, electronic, optical and thermal properties,[1–6] which has led to these 2D materials being promising for new optoelectronic and nanoelectronic applications.[7–10] Recently, antimonene, a monolayer of antimony, was predicted to exhibit a stable geometry and be a semiconductor by density functional theory (DFT).[11] Subsequently, monolayer antimonene has been experimentally achieved on Bi_2Te_3 (111), Sb_2Te_3 (111),[12] or $PdTe_2$ (ref. 13) substrates. Furthermore, an asymmetric washboard structure of antimonene (aW-Sb) was found to maintain its stability at a high temperature of 1000 K, and its armchair and zigzag nanoribbons exhibit excellent electronic properties.

Currently, for the exploration of 2D materials, doping is an effective method to achieve anticipant properties.[14–20] Dai *et al.*[21] investigated the effect of Fe-dopants on β-phase antimonene and found that the Fe-doped system exhibited stable room temperature ferromagnetism (RTFM). He *et al.*[22] and Zhou *et al.*[23] reported 3d transition metal (TM) doped β-phase antimonene, and the results suggested that the doped systems were magnetic semiconductors. Li *et al.*[24] found that electric field and dopants improved the sensitivity to CO molecules of β-antimonene. Yang *et al.*[25,26] investigated the effect of vacancies and 3d-transition-metal doped β-antimonene, and the results indicated that different vacancies and 3d-dopants resulted in different electronic structures and magnetic properties in antimonene. However, few studies explored the effect of dopants on the electronic and magnetic properties of aW-phase antimonene.

Therefore, in this work, we aim to systemically explore the effect of dopants (Ge, Se, Sn, Te, Sc, Ti, V, Cr, Mn, Fe, Co, and Ni) on the properties of aW-phase antimonene using DFT calculations. Firstly, we examined the stabilities of doped systems by calculating the binding energies, charge transfer, and bond lengths. Secondly, we investigated the change of electronic structures. Finally, the magnetic behaviors of doped systems were explored. We hope our results could provide useful information for designing new antimonene-based magnetic and electronic devices.

2. Calculation details and models

All calculations were done with the Vienna *ab initio* Simulation Package (VASP) (VASP).[27–29] The generalized gradient approximation (GGA) using Perdew–Burke–Ernzerhof (PBE) parameterization was used to approximate the exchange-correlation potential,[30] and the Projector-Augmented Wave (PAW) pseudopotentials were employed.[31] A plane-wave basis set with the kinetic energy cutoff is 500 eV and the van ser Waals (vdW) was carried out by D3-Grimme correction (DFT-D3).[32] Considering the localization of 3d TM-dopants, GGA+U is adopted to describe the strong on-site Coulomb interaction. Moreover, the spin–oribit couplings (SOC) act important role in the band structures[33,34] and is also included to calculated the band structures in our study. The convergence criterion between two consecutive steps was set as 10^{-6} eV and a maximum force of 0.001 eV $Å^{-1}$ was allowed on each atom. A 8 × 8 × 1 *k*-point sampling was used for 4 × 4 × 1 antimonene supercells. A vacuum space of 15 Å was set along the out-of-plane direction to avoid the interactions between the neighboring layers. To

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explore the stability of doped systems, the binding energy (E_b) for the doped systems, as follows:

$$E_b = E_{\text{doped-Sb}} - E_{\text{V-Sb}} - E_{\text{dopant}} \quad (1)$$

where $E_{\text{doped-Sb}}$ represents the total energy of the doped antimonene, and $E_{\text{V-Sb}}$ is the energy of antimonene with a single vacancy, and E_{dopant} is the energy of an isolated dopant atom, respectively.

3. Results and discussion

3.1 Geometry structures

Our optimized model of aW-phase antimonene (aW-Sb) is performed in Fig. 1(a) and (b). The lattice constants of a_1 and a_2 are calculated to be 4.28 Å and 4.77 Å, and the nearest-neighbor distances b_1 and b_2 are 2.93 Å and 2.87 Å, respectively. The calculated parameters of geometry structure of aW-Sb are well agreement with previous literatures.[35,36] According to previous reports, aW-Sb is a semiconductor with narrow bandgaps. The band structure of aW-Sb is described in Fig. 1(c). It can be found that it exhibits a indirect band gap of 0.12 eV, which is consistent with previous PBE results.[37,38] We also calculated the bandgap by HSE correction (PBE + HSE) and spin–orbit couplings method (PBE + SOC), and the values are 0.33 eV and 0.03 eV, and the HSE results is larger than PBE result. The SOC result is smaller than PBE result, which is due to the valence band near *Y*-point splits into two bands. Furthermore, the spin-up (majority) and spin-down (minority) channel are represented by black and blue color lines, which are completely symmetrical and the PBE band result is blue color. It suggests the aW-Sb is nonmagnetic. To examine the stability of aW-Sb, the phonon dispersion curves are shown in Fig. 1(d). It can be observed that no imaginary vibrating modes exist, and that illustrates the stability as monolayer antimonene.

To systemically explore the influence of dopant on aW-Sb, we consider 10 types of dopants, including Ge, Se, Sn, Te, Sc, Ti, V, Cr, Mn, Fe, Co, and Ni. The doped aW-Sb structure was created by replacing a Sb atom by a dopant atom, and the doping concentration is 1.56%. Furthermore, the stability of doped systems is examined by the binding energy, and the nearest-neighbor distances between the Sb and dopants (d_1 and d_2) are also summarized in Table 1. The negative binding energies of doped systems indicate the stable geometry structures, and the Ti–Sb is the most stable with a binding energy of −6.40 eV. Moreover, we illustrate one type of optimized doped geometry structures in Fig. 2, namely, Ge–Sb. As shown in Fig. 2 and Table 1, after the doping of Ge, there is no obvious distortion appears

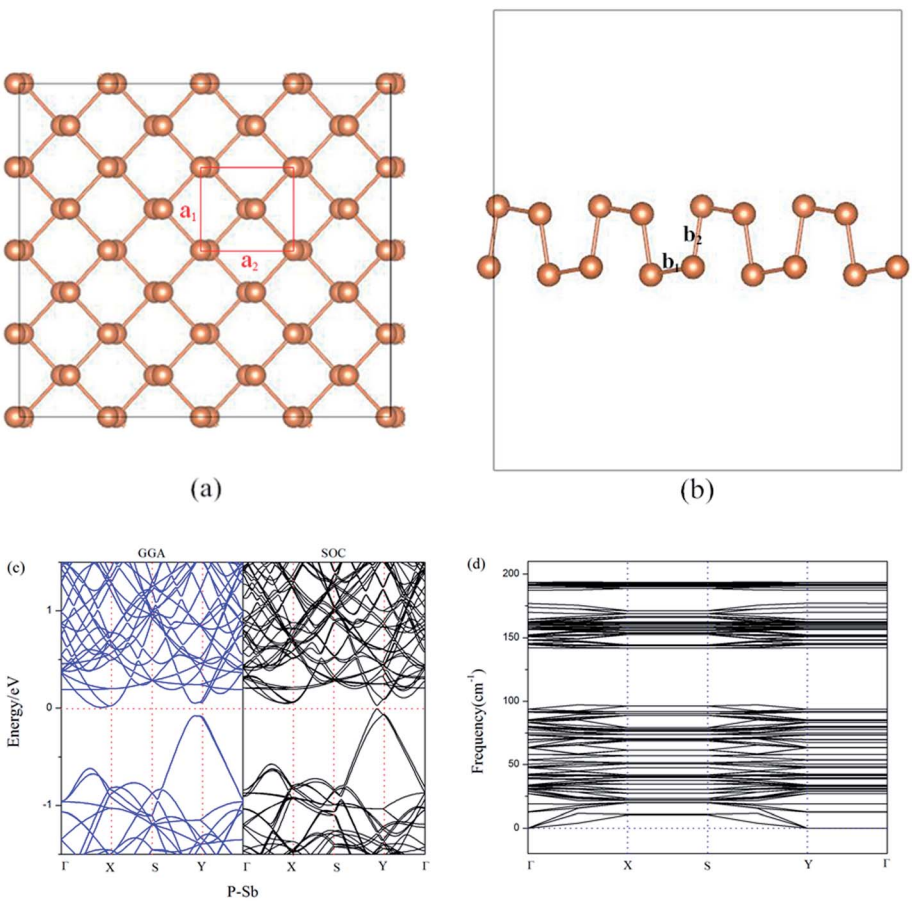

Fig. 1 The top (a) and side (b) view of the optimized structure of pristine antimonene. (c) Band structure and (d) phonon dispersion curves structure of pristine antimonene.

Table 1 Summary of results for doped aW-Sb systems. The properties performed are the nearest band length of the dopant to the two adjacent Sb atom (d_1 and d_2), the binding energy (E_b), the total magnetic moment of doped systems (M_{total}), and the charge transfers of dopants (Q)

Adatom	d_1 (Å)	d_2 (Å)	E_b (eV)	M_{total} (μ_B)	Q (e)
Ge	2.72	2.76	−3.51	0	−0.30
Se	2.76	2.67	−3.51	0	−0.53
Sn	2.91	2.98	−3.24	0	0.18
Te	2.94	2.86	−2.83	0	−0.27
Sc	3.03	2.87	−5.80	0	0.37
Ti	2.87	2.72	−6.40	1.0	0.89
V	2.75	2.67	−5.08	2.7	0.68
Cr	2.73	2.67	−3.75	3.2	0.45
Mn	2.73	2.71	−3.96	3.7	0.42
Fe	2.57	2.50	−4.82	1.3	−0.13
Co	2.49	2.47	−5.88	0	−0.36
Ni	2.55	2.50	−5.70	0	−0.31

and the value of b_1 (2.93 Å) and b_2 (2.87 Å) in pristine aW-Sb change to be 2.72 Å and 2.76 Å. The change of bond lengths of b_1 varied in 0.01–0.44 Å, when that of b_2 is 0.00–0.40 Å. Among the doped structures, the decrease of bond length in Co–Sb was the most obvious. Furthermore, the charge transfer of dopant is calculated by Bader charge analysis.[39] The result indicates that Ge, Se, and Te act as acceptors, while the other dopants are donors. The large charge transfer between the dopants and aW-Sb substrate indicated the strong interaction present, and the Ti-dopant exhibits 0.89e, which is the largest value of Q and is agreement with its largest binding energy. Therefore, the small change of geometry structures, large binding energies and charge transfer are all imply the stability of doped systems.

3.2 Electronic and magnetic properties

To further understand the effect of dopants on the electronic and magnetic structures, we further illustrate the band structure and projected density of states (PDOS) of all doped-Sb systems in Fig. 3 and 4. As performed in Fig. 3, the black and blue color lines represent spin-up and spin-down channels for the PBE results. The PBE results exhibit blue color, when the spin-up and spin-down bands are coincident. We first discuss the GGA (GGA+U) results. As shown in Fig. 3, the doped aW-phase antimonene exhibit metallic, due to the appearance of impurity-band around

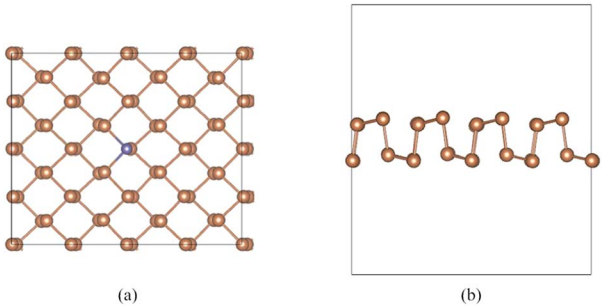

Fig. 2 The top (a) and side (b) view of the optimized structure of Ge-doped antimonene.

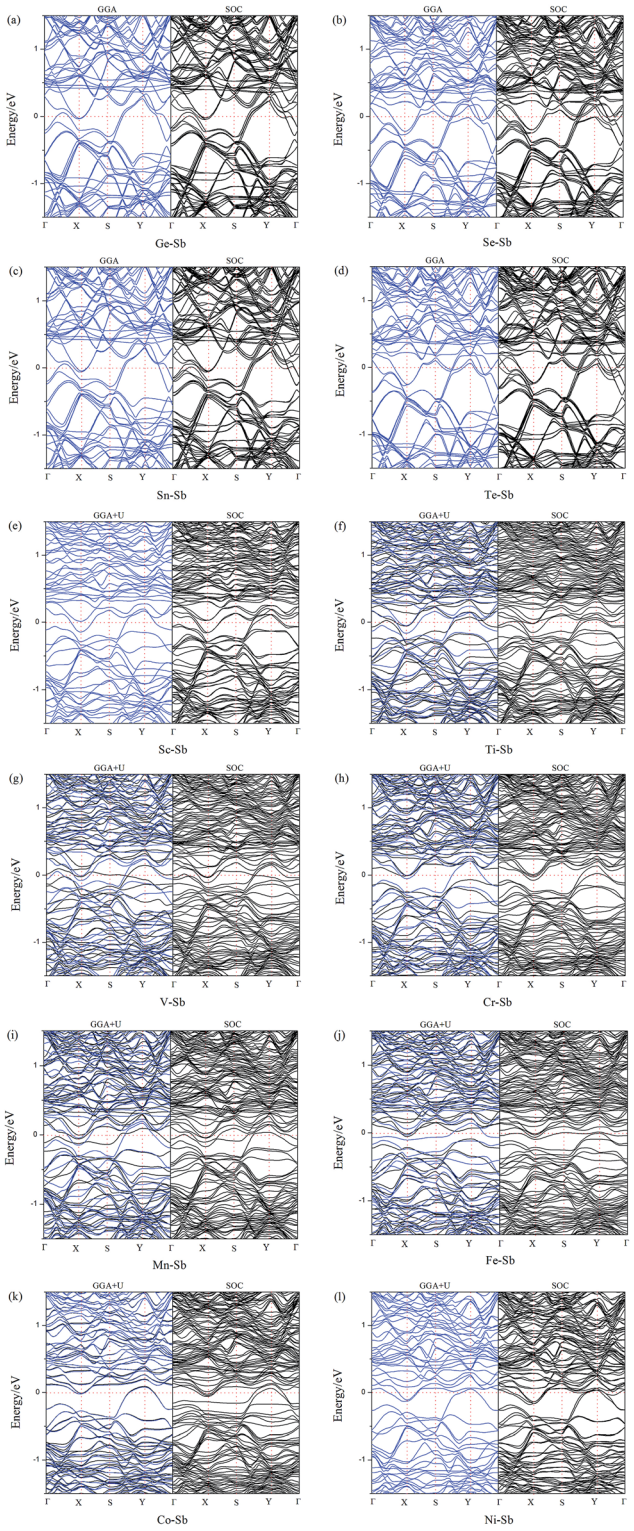

Fig. 3 Band structures of (a) Ge–Sb, (b) Se–Sb, (c) Sn–Sb, (d) Te–Sb, (e) Sc–Sb, (f) Ti–Sb, (g) V–Sb, (h) Cr–Sb, (i) Mn–Sb, (j) Fe–Sb, (k) Co–Sb, and (l) Ni–Sb. For the GGA+U or GGA band structure results, the black and blue colors represent spin-up and spin-down channels, respectively.

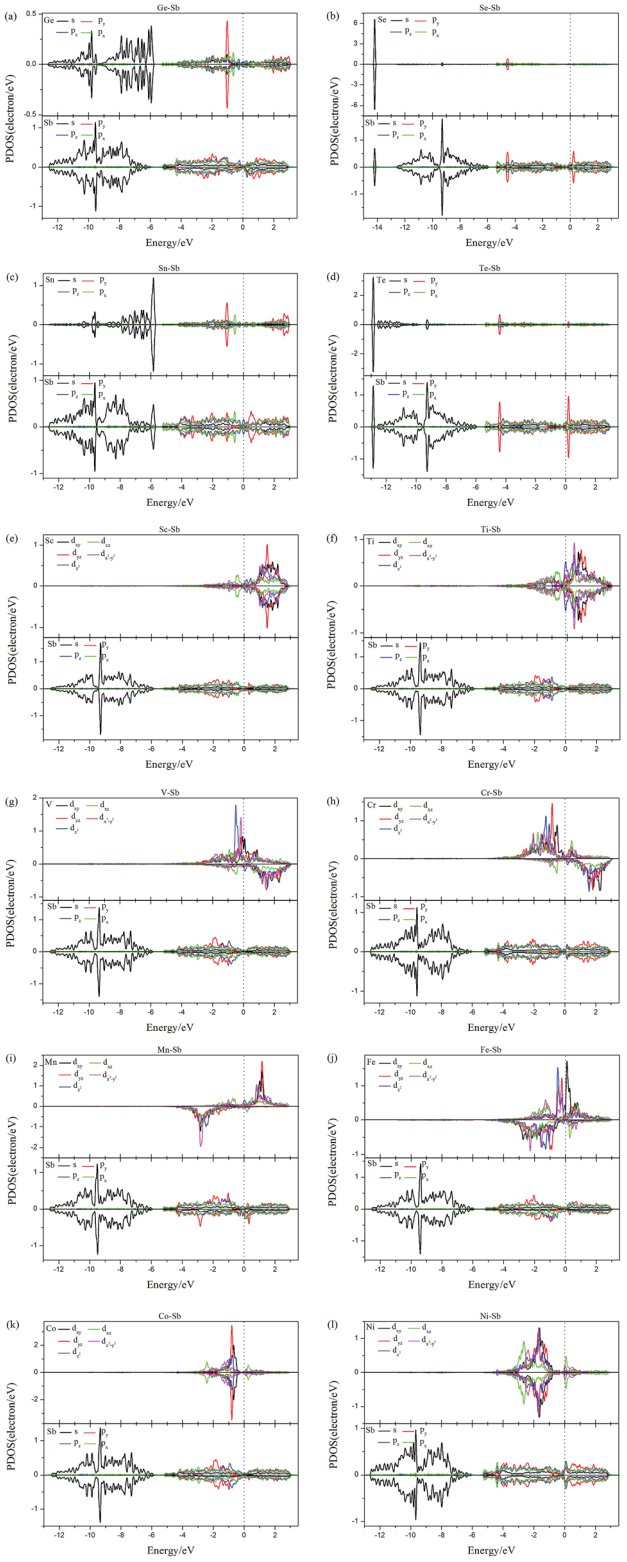

Fig. 4 The PDOS of the dopants and the adjacent Sb atoms around the dopants: (a) Ge–Sb, (b) Se–Sb, (c) Sn–Sb, (d) Te–Sb, (e) Sc–Sb, (f) Ti–Sb, (g) V–Sb, (h) Cr–Sb, (i) Mn–Sb, (j) Fe–Sb, (k) Co–Sb, and (l) Ni–Sb.

the Fermi level contributed by the dopant. We can classify the systems into two types, including weak conductivity and strong conductivity structures. It can be found that only a few channels

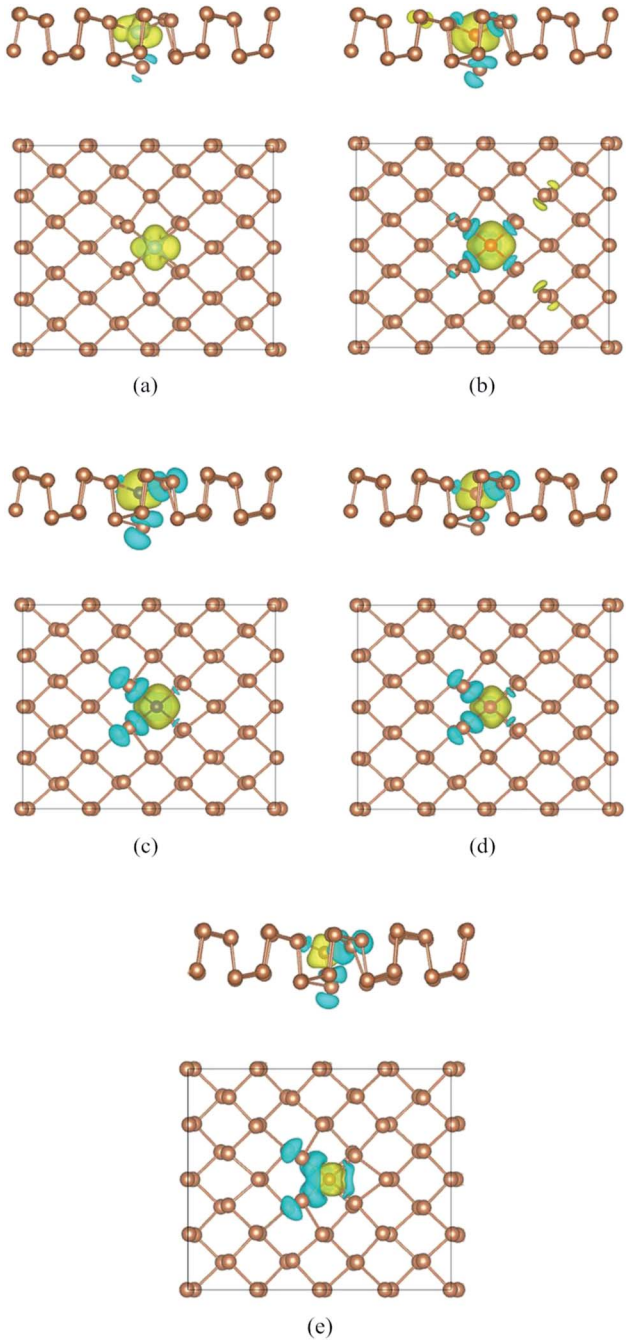

Fig. 5 Top view of spin density of doped antimonene: (a) Ti–Sb, (b) V–Sb, (c) Cr–Sb, (d) Mn–Sb, and (e) Fe–Sb. The isosurface value is set to be 0.0015e Å^{-1}.

of valence or conductive bands go through the Fermi level in Fig. 3(e)–(l) and then the Sc-, Ti-, V-, Cr-, Mn-, Fe-, Co-, and Ni-doped antimonene exhibit weak conductive character. Although, there are more bands through the Fermi level in the Ge-, Se-, Sn-, and Te-doped systems, indicating a character of relative strong conductivity. The pristine aW-phase antimonene is nonmagnetic structure, while the doping of Ti, V, Cr, Mn, and Fe induced magnetic states. As performed Fig. 3(f)–(j), the spin-up and spin-down band channels are unsymmetrical, and we

summary the total magnetic moment of systems in Table 1. For the SOC results, it can be found that the splitting of electronic bands is not obvious, and the shapes of band structures of the doped systems with and without SOC are similar, which is agreement with previous report.[22]

Aiming to deeply explore the contribution of magnetic states, we illustrate the PDOS of dopants and the adjacent Sb atoms in Fig. 4. Firstly, there are obvious hybridization between the dopant and adjacent Sb atoms above and below the Fermi level, which is agreement with the large binding energies and charge transfers, indicating that chemical bonds form and the excellent stability of doped systems. Transition-metal (TM) is well known as magnetic metal. After doping of TM-dopants, the Sc-, Co-, Ni-doped antimonene still maintain nonmagnetic state. It may be resulted from the coupling of unpaired d-orbital electrons of TM-dopants and the p-orbital of adjacent Sb atoms, and that is consistent with the strong hybridization performed in Fig. 4. For the five types of magnetic structures, the d-orbital of dopants dominate the magnetic properties of structures. For example, the unsymmetrical sharp peaks of PDOS in Ti–Sb is mainly contributed by d_{xy} and d_{z^2} orbital, and the magnetic property of Mn–Sb system is dominated by $d_{x^2-y^2}$ and d_{yz} orbital.

To deeply explore the magnetic properties, we also perform the spin density distributions of Ti–Sb, V–Sb, Cr–Sb, Mn–Sb, and Fe–Sb systems in Fig. 5. Firstly, it is obvious that spin density is mainly localized at dopant and adjacent Sb atoms, and that is agreement with the PDOS result (Fig. 4). Secondly, the magnetic moments of dopant are contrary to the adjacent Sb atoms. According to our calculated results, the magnetic moments of Ti-, V-, Cr-, Fe-, and Mn-dopant are 1.1 μ_B, 2.8 μ_B, 3.4 μ_B, 4.1 μ_B, and 2.3 μ_B, while the total magnetic moments of doped structures are 1.0 μ_B, 2.7 μ_B, 3.2 μ_B, 3.7 μ_B, and 1.3 μ_B (Table 1). Therefore, the doping could produce interesting magnetic properties in nonmagnetic aW-phase antimonene.

4. Conclusions

In summary, the geometry stability, electronic and magnetic properties of doped aW-phase antimonene (aW-Sb) have been systemically explored by using density functional theory (DFT) method. The large biding energies and charge transfer between the dopant and antimonene substrate indicate the stable geometry structures of doped systems. The pristine aW-Sb is nonmagnetic semiconductor with a narrow bandgap. After doping, the doped aW-Sb structures all exhibit metallic, and the V-, Cr-, Mn-, Fe-doped systems exhibited different magnetic properties. According to the results of PDOS and spin density distribution, it can be found that the dopant and adjacent Sb atoms dominate the magnetic behavior. Our result is expected to promote the application of antimonene in nanoelectronic devices.

Conflicts of interest

There are no conflicts to declare.

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