Computational Materials Science 156 (2019) 280–285

Contents lists available at ScienceDirect

Computational Materials Science

journal homepage: www.elsevier.com/locate/commatsci

A comparative first-principles study of point defect properties in the layered MX_2 (M = Mo, W; X = S, Te): Substitution by the groups III, V and VII elements

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ARTICLE INFO

Keywords:
Transition metal dichalcogenides
Doping properties
First-principles calculations

ABSTRACT

Dopability in semiconductors plays a crucial role in device performance. Using the first-principles density-functional theory calculations, we investigate systematically the doping properties of layered MX_2 (M = Mo, W; X = S, Te) by replacing M or X with the groups III, V and VII elements. It is found that the defect B_M is hard to form in MX_2 due to the large formation energy originating from the crystal distortion, while Al_M is easy to realize compared to the former. In MoS_2, WS_2 and $MoTe_2$, Al is the most desirable p-type dopant under anion-rich conditions among the group III components. With respect to the doping of the group V elements, it is found that the substitutions on the cation sites have deeper defect levels than those on the anion sites. As_{Te} and Sb_{Te} in $MoTe_2$ and WTe_2 are trend to form shallow acceptors under cation-rich conditions, indicating high hole-concentrations for p-type doping, whereas Sb_S in MoS_2 and P_{Te} in WTe_2 are shown to be good p-type candidates under cation-rich conditions. In despite of that the substitutions of group VII on X site have low formation energies, the transition energies are too high to achieve n-type MoS_2 and WS_2. Nevertheless, for $MoTe_2$, the substitutions with the group VII elements on the anion sites are suitable for n-type doping on account of the shallow donor levels and low formation energies under Mo-rich condition. As to WTe_2, F is the only potential donor due to the shallow transition energy of F_{Te}. Our findings of filtering out unfavorable and identifying favorable dopants in MX_2 are very valuable for experimental implementations.

1. Introduction

Silicon-based semiconductors have dominated the market for a long term, and the further exploration have encountered a bottleneck due to the Moore's law [1]. The extremely high carrier mobility and other unique physical properties of graphene [2] have attracted considerable attention. Since graphene was first synthesized experimentally in 2004 [3], two-dimensional (2D) materials have caused great concern for researchers [2,4–8]. It was ever regarded as the most possible candidate for the replacement of silicon [9]. However, the missing of the band gap in graphene restricts its applications in semiconductor devices [2]. Transition metal dichalcogenides (TMDs) are members of layered materials. It was reported that TMDs have many unique and fascinating optoelectronic properties to fulfill the demands of the applications ranging from spin-related to photoelectric devices [2]. Moreover, TMDs possess a finite band gap whose value depends on the thickness of the materials in the grown-direction [10,11]. For example, monolayer MoS_2 has a direct band gap over 1.9 eV, while the corresponding multilayer counterpart shows an indirect band gap [11]. The intriguing properties make TMDs becoming very attractive and a series of work has been published in the past decades [4,11–14]. Dopability plays a crucial role in the application of optoelectronic devices [15–17]. Therefore, a sufficient understanding of the doping properties of TMDs is of great importance.

There are two main factors to determine the dopability of a material [18]. One is the solubility of the dopants which depends significantly on the selected atoms and the growth conditions. Another important factor is the defect transition level which should not be ionized at working temperatures for practical applications. Both factors are dependent on the selected doping atoms, and therefore can be controlled in principle by choosing the appropriate dopants and building the reliable growth environments. Recently, doping of TMDs has been widely reported by several groups [4,19–21]. For example, it is reported that doping in MoS_2 could not only tune the energy band gap in a wide range [11], but

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https://doi.org/10.1016/j.commatsci.2018.10.004
Received 4 May 2018; Received in revised form 28 September 2018; Accepted 4 October 2018
0927-0256/

also change the materials from n-type to p-type transition according to the selection of the dopant atoms. Komsa et al. have systematically investigated the native defects in MoS_2, and found that the S vacancies are the most abundant defects [19]. Xia et al. reported that halogen atoms can increase electron concentration when doping on SnS_2 monolayers [22]. Noh et al. believed that S vacancy is a deep acceptor and Mo interstitial is a deep donor in MoS_2 [23]. Lin et al. have classified structural defects of TMDs, and found that S vacancy has the lowest formation energy of native point defects [16]. Those studies are primarily concentrated on the intrinsic structural defects, while the effect of substitutional doping of TMDs has not been well-studied.

In this paper, we investigate systematically the doping properties of layered MX_2 by replacing M or X with the groups III, V and VII elements, where M = Mo, W and X = S, Te. Based on the first-principle density-functional theory, we calculate the defect formation energies and the transition levels of MX_2. On the other hand, to confirm our results, we have also used the Janak's theorem to calculate the defect transition levels [24]. It is found that for MoS_2, in despite of that the substitutions of group VII on X site have the low formation energies, the transition energies are too high to achieve n-type doping. For p-type doping, both Al_{Mo} and Sb_S exhibit low transition energies, although Al_{Mo} favors S-rich condition and Sb_S favors Mo-rich condition. In WS_2, Al_W has low formation and transition energies under S-rich condition, suggesting Al can be a promising candidate for p-type doping. For $MoTe_2$, it is shown that the substitutions with the group VII elements on the Te site are suitable for n-type doping, while As_{Te} and Sb_{Te} are shallow acceptors corresponding to the p-type doping under Mo-rich condition. As to WTe_2, due to the low formation energy and shallow transition energy, F_{Te} acts as a donor under W-rich condition, while P_{Te}, As_{Te} and Sb_{Te} are good acceptors under W-rich condition, and also Al_W under Te-rich condition. Our results are useful for the identification of external impurities with respect to either n-type or p-type in TMDs, and therefore reduce the cost in materials synthesis and improve the efficiency in experiments.

2. Computational method

In order to investigate the electronic properties of the layered MX_2, we perform the band structure and total energy calculations by using first-principle density-functional theory as implemented in VASP-code [25,26]. We use the general-gradient approximation (GGA), and the Perdew-Burke-Ernzerh functional (PBE) for the exchange and correlation potentials is adopted [27,28]. The core-valence interactions are modeled within the framework of the projector-augmented wave method [29]. The cut-off energy for the plane-wave expansion is set as 400 eV. The energy threshold for convergence is set as 10^{-4} eV. The layered MoS_2, WS_2, $MoTe_2$ and WTe_2 are modeled by $4 \times 4 \times 1$ supercell which contains 96 atoms. For charged defects, a uniform background charge is added to keep the global charge of the system neutrality [18]. To relax the structure, Brillouin-zone sampling is performed within the Monkhorst-Pack special k-mesh method [30] and a $3 \times 3 \times 3$ grid is used. The optimal atomic positions are determined by minimizing the total energy of the system and the Hellman-Feynman forces acting on individual atoms are less than 0.02 eV/Å.

After relaxation, the defect formation energy $\Delta H_f(\alpha, q)$ and transition levels are determined according to Refs. [18,31–33]. To calculate $\Delta H_f(\alpha, q)$ we have to compute the total energy $E(\alpha, \mathrm{q})$ for a supercell containing the defect α in charge state q, the total energy $E(\mathrm{host})$ for the same supercell without the defect, and the total energy of the involved elemental solids or gases at the stable phase. Since the formation energy depends on the electron Fermi level E_F, for a given system with defect α and in charge state q, it reads

$$\Delta H_f(\alpha, q) = \Delta E(\alpha, q) + \sum_i n_i \mu_i + qE_F \tag{1}$$

where $\Delta E(\alpha, q) = E(\alpha, q) - E(\mathrm{host}) + \sum n_i E_i + q\varepsilon_{VBM}(\mathrm{host})$, μ_i is the chemical potential of the constituent i referred to the elemental solid/gas with energy E_i, $\varepsilon_{VBM}(\mathrm{host})$ is the valence band maximum (VBM) energy of the host, n_i represents the number of elements, and q describes the number of electrons transferred from the supercell to the reservoirs. In addition, μ_M and μ_X in Eq. (1) are not independent and limited by the formation of the stable MX_2: $\mu_M + \mu_X = \Delta H_e(MX_2)$, where$\Delta H_e(MX_2)$ is the enthalpy of the compound MX_2. Our calculated formation enthalpies shown in Table 1 are compared with the experimental data. One can see that they are in good agreement. Finally, the defect transition energy is determined by the Fermi energy at which the formation energy for the defect α at charge state q is equal to that at charge state q':

$$\varepsilon(q/q') = [\Delta E(\alpha, q) - \Delta E(\alpha, q')]/(q' - q) \tag{2}$$

Table 1

The calculated lattice constant a (Å), band gap E_g (eV) and formation enthalpy ΔH_e (eV) of the layered MX_2, where the corresponding experimental data is listed for comparison.

	a^{cal}	a^{exp}	$E_g{}^{cal}$	$E_g{}^{exp}$	$\Delta H_e{}^{cal}$	$\Delta H_e{}^{exp}$
MoS_2	3.19	3.16 [34]	1.27	1.29 [35]	−2.64	−2.45 [36]
WS_2	3.15	3.15 [37]	1.51	1.35 [38]	−2.47	−2.50 [39]
$MoTe_2$	3.55	3.52 [37,38]	1.02	0.95 [38]	−0.92	−0.93 [40]
WTe_2	3.55	3.60 [41]	1.00	–	−0.20	−0.34 [42]

In the following by using Eqs. (1) and (2) we calculate the defect properties of the layered MX_2 with the substitution of M or X by the groups III, V and VII elements.

3. Results and discussion

The layered MX_2 has hexagonal lattice with honeycomb structure as shown in Fig. 1, where both the top (a) and side (b) views are presented and different colors indicate various types of atoms. The coupling between MX_2 monolayers is by weak van der Waals interaction. The space group of MX_2 is $P6_3/mmc$. The lattice constants, band gaps, as well as the formation enthalpies of MX_2 are given in Table 1, and the corresponding experimental values are subsequently listed as a comparison. The convergence of our results is confirmed. It is found that both the theory and experiments show good agreement, which indicates to some extent that the GGA-PBE captured the valence electrons properly. We therefore do not apply the advanced hybrid functional calculations, since it is indeed time-consuming for a supercell simulation. In our study, all dopants are chosen from the groups III, V and VII elements and therefore the substitution happens by replacing M or X atoms. Fig. 2 shows the calculated formation energies for the substitutional defects as a function of Fermi energy in MX_2 under anion-rich and cation-rich conditions, and the explicit data of $\Delta H_f(\alpha, 0)$ is presented in Table SI in supplementary materials for the system in neutral state at $\mu_D = 0$, where μ_D decribes the chemical potential of the dopants.

In Fig. 2, we show the formation energies represented by the red[1] lines for the substitutions on the cation sites by the group III elements. It is clearly seen that B_M has a high formation energy in all the p-type MX_2. On one hand, it is due to the large mismatch of the atomic radius between B (r = 0.81 Å) and Mo (1.40 Å) or W (1.41 Å), which leads to a large distortion after the structure relaxation as shown in Fig. 1(d). To eliminate the external strains, additional energy must be paid. Therefore, the system prefers to form a low-symmetry configuration. Fig. 1(c) and (d) shows the atomic configurations of the defected structures after relaxation by switching the symmetry on and off, respectively. One can see that distinct from the case of (c), the boron in (d) deviates significantly, where the bond lengths and bond angles are presented. On

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[1] For interpretation of color in Fig. 2, the reader is referred to the web version of this article.