First-principles studies of transition metal defects in a MoS_2 monolayer

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Abstract. Density functional theory (DFT) implemented within the Vienna *ab-initio* simulation package (VASP), have been used to study the effects of transition metal defects (Rhenium (Re) and Tantalum(Ta)) on the thermodynamic stability and electronic properties of a MoS_2 monolayer. Calculations are performed using the projector augmented wave method (PAW) with the Perdew-Burke-Ernzerhof (PBE) for the exchange-correlation interactions. Our results show that Ta_{Mo} is a thermodynamically stable $p-$type defect whereas Re_{Mo} is a $n-$type with high cost of energy. To reduce the high energy cost of Re_{Mo} in a MoS_2, co-doping was considered. Our studies show that the co-doping of acceptors and donors to be accessible, the acceptors should dominate the donors. The variation of donors and acceptors in a MoS_2 monolayer tune the magnetic moment on and off. Our results indicate that combination of p-type (Ta) and n-type (Re) doped MoS_2 monolayers are promising materials for various electronic applications.

1. Introduction

Since its discovery, graphene has attracted considerable attention due to its unique electronic structure, high carrier mobility and exceptional strength [1]. Although it is a promising material for nanoelectronic devices, the absence of band gap inhibits its direct application. For this reason, researchers became interested in exploring other kind of two dimensional (2D) materials. The transition metal dichalcogenides (TDMCs) such as MoS_2, WS_2, $MoSe_2$, WSe_2, etc, are wide band gap semiconductors and are thermodynamically stable 2D materials [2]. Several studies have reported that MoS_2 monolayer has a band gap of about 1.90 eV experimentally [3] and of about 1.67 eV theoretically [4, 2]. Xu *et al.* reported that MoS_2 exhibits an excellent carrier mobility and desirable optical properties. These interesting properties make MoS_2 a suitable candidate for nanoelectronic devices [5].

During the synthesis of MoS_2 monolayer, point defects and impurities appear in the samples [6] just like in any materials. The presence of these defects are known to greatly alter the properties of pristine MoS_2 monolayer. It was reported that presence of the $p-$type and $n-$type defects causes semiconductor to metal transition in a MoS_2 system. Noh *et al.* reported that Rhenium (Re) impurities exist naturally in a MoS_2 monolayer and are $n-$type defects [7]. The valence band maximum (VBM) and conduction band minimum(CBM) states of a pristine MoS_2 monolayer are derived mainly from Mo $4d$ orbitals. This was shown by atomic resolution transmission electron microscopy [8]. In most studies of defects in a MoS_2 monolayer, Mo site is chosen in order to examine the influence of defects on the VBM and CBM states.

The widely studied $p-$type defect in MoS_2 is the Niobium (Nb) substituting Molybdenum (Nb_{Mo}). Dolui *et al*. reported that the presence of Nb_{Mo} has low formation energy and introduces impurity states above the VBM whose origin is the hybridisation of Nb and Mo d orbitals [9]. Lu *et al*. reported that the formation energy for Ta_{Mo} is lower than that of Nb_{Mo}. However, its electronic and magnetic properties have not been explored extensively [10]. Therefore, Tantalum (Ta) which is below Nb on the periodic table is also worth of investigation as an isolated defect (Ta_{Mo}) to learn how its interaction with MoS_2 influences the electronic and magnetic properties of MoS_2 monolayer.

In this paper, we examine the effect of Ta acceptor and Re donor defects on the thermodynamic stability and electronic properties of a MoS_2 monolayer. We also examine Ta and Re co-doping on MoS_2 monolayer. This will be to study the interaction of an acceptor (Ta) and donor (Re) defects on the stability and electronic properties of the system. We further identify Ta-Re configurations that have ferromagnet characteristics and low formation energy which will be important in spintronic application devices.

2. Methodology

In this work, density functional theory (DFT) [11] as implemented in the Vienna $ab-initio$ simulation package(VASP) [12] is employed to perform ab initio calculations on the electronic and magnetic properties of monolayer MoS_2 doped with Re and Ta impurities. All calculations are carried out using the projector augmented wave (PAW) pseudopotential and generalized gradient approximation (GGA) exchange correlation parameterized by Perdew, Burke, and Ernzerhof (PBE) [13]. A 5×5 hexagonal supercell with 75 atoms (25 Mo atoms and 50 S atoms) and having a vacuum region of 15 Å is employed to suppress the influence of neighboring layers. A kinetic energy cutoff of 250 eV for plane wave expansion and 2×2×1 k-point mesh are used. The atomic structures were relaxed until the Hellmann-Feynman forces were less than 0.02 eV/Å. The formation energies (E_{form}) of a particular dopant is defined as :

$$E_{form} = E_{tot}[MoS_2 + D] - E_{tot}[MoS_2] + \mu_{host} - \mu_D \; [6] \tag{1}$$

where $E_{tot}[MoS_2+D]$ is the total energy of the MoS_2 monolayer with the substitutional atom D (Re or Ta), $E_{tot}[MoS_2]$ is the total energy of the pristine MoS_2 monolayer. μ_D and μ_{host}, are respectively the chemical potentials of the substitutional atom D (Re or Ta) and the host atom (Mo or S). All the chemical potentials are calculated by using the reference (stable) phase of each element. The orthorhombic structure is chosen for the sulphur and body center cubic (bcc) for Mo. μ_D is obtained from DFT total energies of a Ta bcc metal and Re hexagonal structure per atom.

3. Results and discussion

Before discussing the effect of dopant on a MoS_2 monolayer, let us analyse the electronic properties of the pristine MoS_2 monolayer. The top view and side view of a MoS_2 monolayer are shown in (Fig. 1). It can be seen that each of the S atom is bonded covalently to the three Mo atoms. Each Mo atom is coordinated with six S atoms, three of them make the top surface and other three to the bottom S layer. The band gap obtained using GGA functional for the pristine is 1.65 eV. This value is in good agreement with the experimental value of 1.90 eV and the previous theoretical results found in references [4, 2]. The VBM is mainly constituted from the hybridisation of Mo 4d and S 3p orbitals, whereas the CBM is mainly due to Mo 4d orbitals. The pristine of MoS_2 monolayer is a non-magnetic material in nature, since the spin up states are invertibly symmetric to spin down states for the entire plot. In the next section, we examine the effects of Ta and Re atoms on the electronic properties of a MoS_2 monolayer.

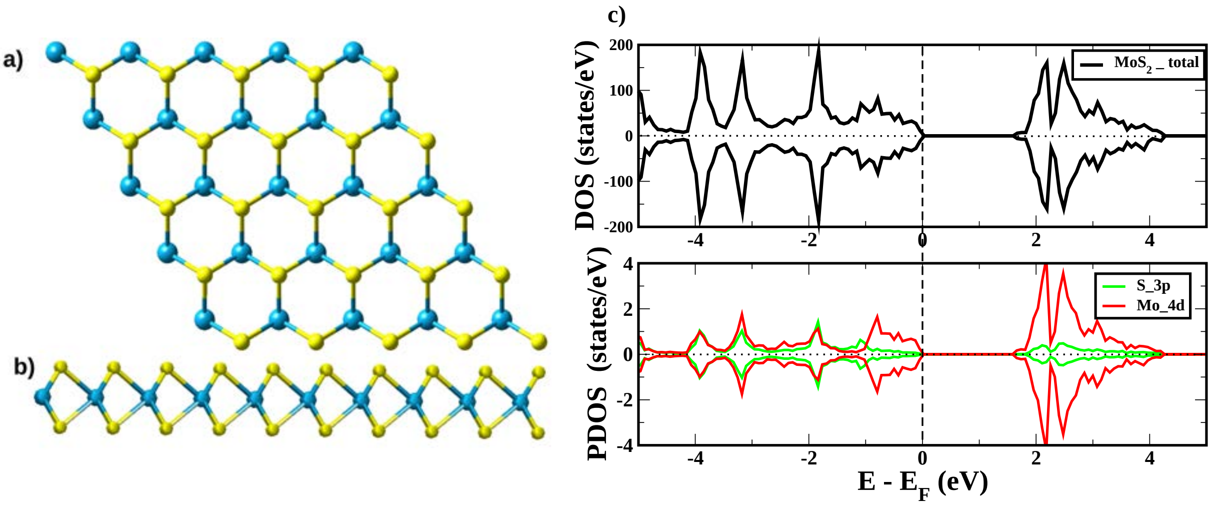

Figure 1. (a) Top view and (b) side view of a 5×5 MoS_2 monolayer. Blue spheres indicate Mo atoms and light yellow spheres indicate S atoms. (c) The total DOS and Projected DOS for a pristine MoS_2 monolayer. The positive DOS and PDOS values refer to majority spins, while the negative ones are for minority. The dashed line indicates the Fermi energy.

3.1. Ta substitution

Firstly, we analyse Ta atom(s) substituting Mo atom(s). The number of Ta dopants considered ranges between one and three (Ta_x where $x =$ 1Mo, 2Mo and 3Mo) on a single hexagonal ringlike in a MoS_2 monolayer. When examining the structures, we found that the insertion of Ta atom in a MoS_2 monolayer affects the bond lengths. The relaxed Ta-S bonds for Ta_{1Mo}, Ta_{2Mo} and Ta_{3Mo} are 2.41, 2.46 and 2.47 Å respectively. The Mo-S bond length for the relaxed MoS_2 monolayer is 2.42 Å which is in good agreement with references [2, 9]. Therefore, we realise that the induced strain in Ta_{1Mo} is small, however in Ta_{2Mo} and Ta_{3Mo}, it is significantly large. This should have a significant effect on the other properties.

Table 1. Formation energies E_{form} (eV) and magnetic moments $m(\mu_B)$ of Ta and Re defects in a MoS_2 monolayer.

Type of doping	E_{form}(eV)	$m(\mu_B)$
Ta_{1Mo}	-0.43	0.01
Ta_{2Mo}	-0.97	0.00
Ta_{3Mo}	-1.73	0.00
Re_{1Mo}	2.18	1.00
Re_{2Mo}	4.02	0.00
Re_{3Mo}	5.73	1.00
$Ta_{1Mo}Re_{1Mo}$	0.09	0.01
$Ta_{2Mo}Re_{1Mo}$	-0.38	0.01
$Ta_{1Mo}Re_{2Mo}$	2.10	0.98

The relative stability of our defects is determined using the formation energies calculated using Eq.1. Table.1 shows that the formation energies of Ta_{Mo} (Ta_{1Mo}, Ta_{2Mo} and Ta_{3Mo}) are all negative. We realised that E_{form} becomes more energetically favourable when the number of defects increases. The negative formation energies indicate that the corresponding substitutional reactions can occur spontaneously under favourable conditions. Ding *et al.* have reported that

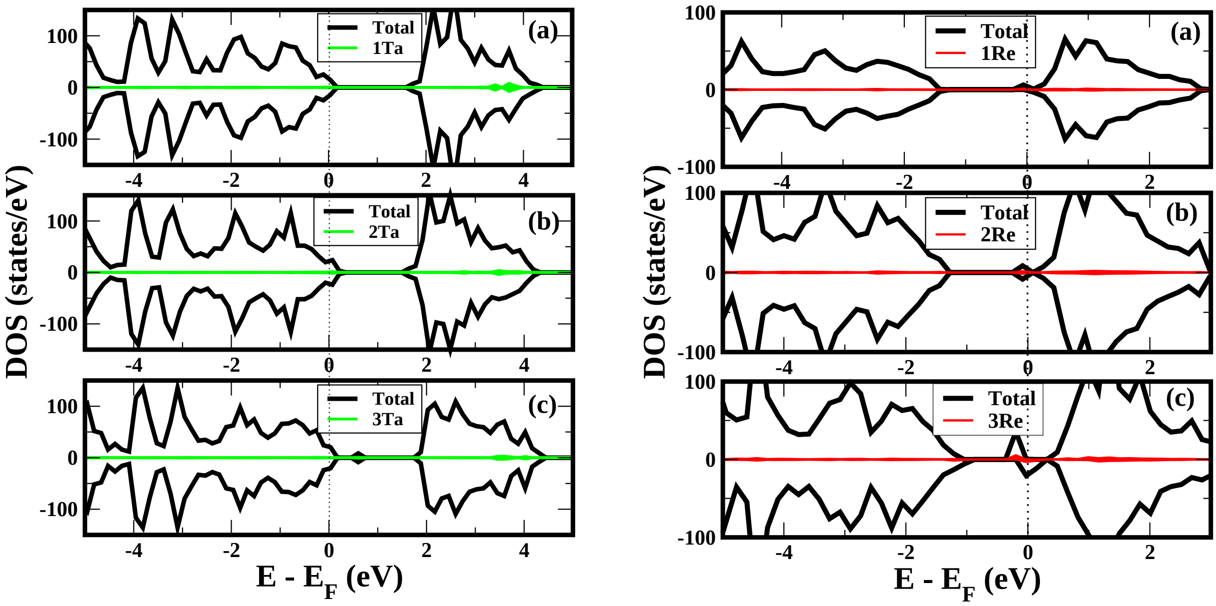

Figure 2. The Total DOS for a 5×5 supercell of (a) Ta_{1Mo}, (b) Ta_{2Mo}, (c) Ta_{3Mo}, (d) Re_{1Mo}, (e) Re_{2Mo} and (f) Re_{3Mo}. The positive DOS values refer to majority spins, while the negative ones are for minority. The dashed line indicates the Fermi energy.

Fig. 2 shows the density of states (DOS) plots for Ta_{1Mo} (Fig. 2(a)), Ta_{2Mo} (Fig. 2(b)) and Ta_{3Mo} (Fig. 2(c)). We found that the effect of Ta substituting Mo is to shift the Fermi level into the valence band. This shift is an indication that Ta_{1Mo}, Ta_{2Mo} and Ta_{3Mo} systems have deficiency of electrons compared to MoS_2. Therefore, Ta_{Mo} systems are p-type defects in a MoS_2 monolayer and can act as an electron trap. In a Ta_{3Mo} DOS, we also noted an extra non-spin polarised impurity states at 0.47 eV above the VBM within the band gap. These exotic impurities states are relative deep, and therefore will unlikely be ionised at room temperature [14]. Fig. 2 also shows that in all cases, the minority spin is aligned to the majority spin revealing that the systems are non-magnetic (see Table.1). Nevertheless, Ta defect is energetically stable and can be a suitable p-type dopant for MoS_2 monolayer.

3.2. Re substitution

The formation energies of Re defect configurations, Re_{1Mo}, Re_{2Mo} and Re_{3Mo}, are shown in Table.1. They are all positive indicating that the cost of substituting Mo with Re is energetically expensive. We further found that when the number of Re dopants in the system increases, i.e Re_{3Mo}, the system gradually becomes more energetically unstable. The DOS of Re_{1Mo}, Re_{2Mo} and Re_{3Mo} are shown in Fig. 2(a), Fig. 2(b) and Fig. 2(c) respectively.

For Re_{1Mo} system, we found that the induced defect state is near but at 0.25 eV below the CBM . This state is formed by hybridisation of the Re 5d orbitals with the Mo 4d orbitals. The creation of Re_{1Mo} add an electron into the system, resulting in shifting the Fermi level into the CB. This reveals that Re_{1Mo} system is a $n-$type. The DOS of Re_{1Mo} (Fig.2(d)) also shows that the majority spin and minority spin are asymmetric leading the system been magnetic with a magnetic moment of $1\mu_B$. This is in good agreement with reference [9].

The substitution of two Re dopants induces non-spin polarised states at 0.19 eV below the CBM. This system is non-magnetic in nature. This might be due to the effect of pairing of localised electrons each contributed by defect. However, the introduction of three Re defects for the Re_{3Mo} system induces spin-polarised states in the gap around 0.3 eV below the CBM. A magnetic moment of $1\mu_B$ in this defective system is noted. The half metallic character is also noted in Re_{3Mo} as the Fermi level crosses only the spin down states. The systems that are half metallic ferromagnet have a future application in the spintronic technology.

Since the intrinsic defects are inefficient to create a $n-$type MoS_2 monolayer [9], our results indicate that Re is a plausible for a $n-$type dopant in MoS_2 although highly expensive to form.

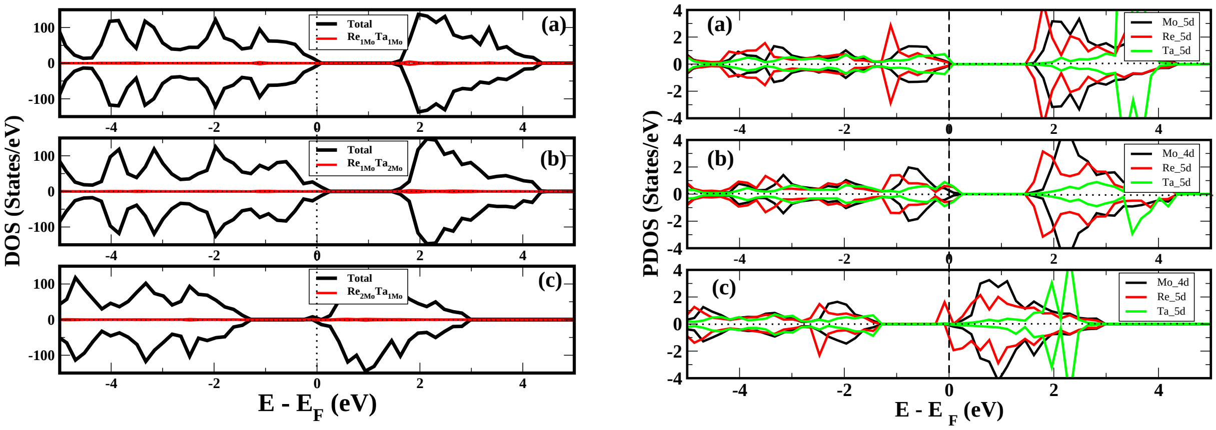

Figure 3. The total DOS(left) and Projected DOS(right) for (a) $\mathrm{Ta}_{1Mo}\mathrm{Re}_{1Mo}$, (b) $\mathrm{Re}_{1Mo}\mathrm{Ta}_{2Mo}$ and (c) $\mathrm{Re}_{2Mo}\mathrm{Ta}_{1Mo}$. The dashed line indicates the Fermi energy.

3.3. Re and Ta co-doping

Lastly, we examine the co-doping of the Re and Ta dopants in a MoS_2 monolayer. It has been reported that Re exists spontaneously during the synthesis of the MoS_2 samples and an $n-$type device was characterised. We model the interactions of naturally existing Re defects with Ta dopants in a MoS_2 system. This will be to give an explanation of how the unintentional donors can be controlled by acceptors in a MoS_2 monolayer.

Substitution around the ringlike hexagonal is considered by varying the number of dopants. The three possible defects denoted as $\mathrm{Re}_{1Mo}\mathrm{Ta}_{1Mo}$, $\mathrm{Re}_{1Mo}\mathrm{Ta}_{2Mo}$ and $\mathrm{Re}_{2Mo}\mathrm{Ta}_{1Mo}$ are considered. Table.1 shows that the formation energies of these defects are higher than that of isolated acceptors (Ta) doping but lower than that of donors (Re) doping. The relatively low formation energy for $\mathrm{Re}_{1Mo}\mathrm{Ta}_{1Mo}$ of 0.09 eV albeit positive, do not rule out the possibility of synthesising this material at an ambient conditions. The substitution of a second acceptor making $\mathrm{Re}_{1Mo}\mathrm{Ta}_{2Mo}$ system yields a low formation energy of -0.38 eV. However two donors and one acceptor $\mathrm{Re}_{2Mo}\mathrm{Ta}_{1Mo}$ is a problem because the formation of this system is endothermic. For such defects to be easily accessible under ambient conditions, acceptors should always dominate the donors.

For the first case of $\mathrm{Re}_{1Mo}\mathrm{Ta}_{1Mo}$, the DOS is quite similar to the pristine (Fig. 3(a)). Since Re has one electron more and Ta has one electron less compared to Mo, those two excess electrons compensate each other. Therefore, the compensation does not alter much the electronic behaviour of the MoS_2 monolayer. But for $\mathrm{Re}_{1Mo}\mathrm{Ta}_{2Mo}$, we observe that the Fermi level is shifted deeper into the VB. This is to ensure that $\mathrm{Re}_{1Mo}\mathrm{Ta}_{2Mo}$ behave as $n-$type material. The system is, however, non-spin polarised with no magnetic moment obtained.

In the case of $\mathrm{Re}_{2Mo}\mathrm{Ta}_{1Mo}$, impurities states appear near the CBM. They are originated from 5d orbital of Re (Fig. 3(a)). The Fermi level is shifted closer to the CBM which indicates that $\mathrm{Re}_{2Mo}\mathrm{Ta}_{1Mo}$ has a p-type behaviour. After the compensation of one electron from Re and one from Ta, there is still one unpaired electron in the system which makes the system ferromagnetic with a magnetic moment of $1\mu_B$.

4. Conclusion

We have successfully studied the electronic properties and the thermodynamic stability of a MoS_2 monolayer doped with Re and Ta atoms using DFT approximation. We considered isolated doping along a single hexagonal ringlike in a 5×5 supercell of MoS_2 monolayer. We found that Ta atom doping is thermodynamically stable (exothermic) for all possible defect configurations. Ta doping also show a $p-$type features in MoS_2 monolayer. For Re doping, the formation energies are positive (endothermic) for all defect configurations considered. For Re_{1Mo} and Re_{3Mo} the system show ferromagnetic features with a magnetic moment of about $1\mu_B$. The DOS analysis of Re doping possess $n-$type characteristics. In trying to control or lower the high formation energy of Re doping co-doping of Ta with Re was also considered. This was to combine donors (Re) with acceptors (Ta) in a MoS_2 monolayer. Three configurations were investigated $\mathrm{Ta}_{1Mo}\mathrm{Re}_{1Mo}$, $\mathrm{Re}_{1Mo}\mathrm{Ta}_{2Mo}$ and $\mathrm{Re}_{2Mo}\mathrm{Ta}_{1Mo}$. $\mathrm{Re}_{Mo}\mathrm{Ta}_{2Mo}$ is the most energetically favourable configuration whereas $\mathrm{Re}_{2Mo}\mathrm{Ta}_{1Mo}$ is the least. For a co-doping to be releasable under ambient conditions, acceptors should dominate the donors. Our results suggest that these systems might be useful in various electronic and spintronic devices applications.

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References

[1] Geim A K and Novoselov K S 2007 *Nat. Mater.* **6** 183–191
[2] Ding Y, Wang Y, Ni J, Shi L, Shi S and Tang W 2011 *Phys.* B **406** 2254–60
[3] Izyumskaya N, Demchenko D O, Avrutin V, Özgür Ü and Morkoç H 2014 *Turk. J. Phys.* **38** 478–496
[4] Faraji M, Sabzali M, Yousefzadeh S, Sarikhani N, Ziashahabi A, Zirak M and Moshfegh A 2015 *RSC Adv.* **5** 28460–66
[5] Xu M, Liang T, Shi M and Chen H 2013 *Chem. Rev.* **113** 3766–98
[6] Komsa H P and Krasheninnikov A V 2015 *Phys. Rev.* B **91** 125304
[7] Noh J Y, Kim H and Kim Y S 2014 *Phys. Rev.* B **89** 205417
[8] Lin Y C, Dumcenco D O, Komsa H P, Niimi Y, Krasheninnikov A V, Huang Y S and Suenaga K 2014 *Adv. Mater.* **26** 2857–61
[9] Dolui K, Rungger I, Pemmaraju C D and Sanvito S 2013 *Phys. Rev.* B **88** 075420
[10] Lu S C and Leburton J P 2014 *Nanoscale Res. Lett.* **9** 1–9
[11] Kohn W and Sham L J 1965 *Phys. Rev.* **140** A1133
[12] Hafner J 2008 *J. Comput. Chem.* **29** 2044–78
[13] Perdew J P, Burke K and Ernzerhof M 1996 *Phys. Rev. Lett.* **77** 3865
[14] Freysoldt C, Grabowski B, Hickel T, Neugebauer J, Kresse G, Janotti A and Van de Walle C G 2014 *Rev. Mod. Phys.* **86** 253