Monolayer Tungsten Disulfide with Transition Metal Doping

C.-Y. Chen[1,2], Y. Li[1,2,3]
[1]*Parallel and Scientific Computing Laboratory;* [2] *Institute of Communications Engineering;*
[3]*Department of Electrical and Computer Engineering, National Chiao Tung University, 1001 Ta-Hsueh Rd., Hsinchu 300, Taiwan*
ymli@faculty.nctu.edu.tw

In this work, monolayer tungsten disulfide (mWS_2) doped by various 3d transition metals (TM), with two different concentrations, 7.13×10^{13} and 2.85×10^{14} cm^{-2}, are studied by density-functional-theory simulation. Not like many studies assuming substitutional doping sites [1-2], we considered two interstitial (I−) and two substitutional (S−) sites. Then, the work function, the charge transfer, and the projected local density of state are accordingly discussed.

This study uses Vienna ab initio Simulation Package (VASP) [3] to calculate structure relaxation and electronic properties under spin-polarized density functional theory (DFT). Perdew-Burke-Ernzerhof (PBE) is used as an exchange-correlation function since our intensive accuracy test before [4-5], as shown in Fig. 1. The cutoff kinetic energy is 500 eV; the force acting on each atom of relaxed structure is smaller than 0.01 eV/A^o; the energy difference is less than 10^{-6} per atom.

Figure 2 shows the simulation flow. The calculated band structures of Fig. 2(a) bulk and Fig. 2(b) monolayer WS_2 are verified with experimental results. To determine the most stable site with lowest formation energy, four possible doping sites, two interstitial (I−) and two substitutional (S−) sites, are discussed. The formation energy is determined with the formula in Fig. 3. The interstitial site, I−T, has the lowest formation energy for all TM dopant in this study, as shown in Fig. 4.

The formation energy for all TM dopant are listed in Tab. I. The calculated magnetic moments are listed in Tab. II, doping with scandium (Sc) and copper (Cu) results in large change of magnetic moment, about 61.7% and 89% reductions, as doping concentration increases. Figure 5 plots the work function of TM-doped mWS_2 with respect to two concentrations. The titanium (Ti)-doped mWS_2 has the lowest work function while zinc (Zn)-doped has the highest work function. Doping with Sc possesses the largest range of modulation of work function, about 1.63 eV, among different doping species. The difference between conduction band and fermi energy is discussed in Fig. 6. Ti-doped mWS_2 behaves metal; Sc, manganese (Mn), and Chromium (Cr) are suitable for n-type dopant; and nickel (Ni) and Zn are for p-type dopant.

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References:

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Kohn-Sham Equation:

$$\left(\frac{p^2}{2m} + V_{\text{nucl}}(\mathbf{r}) + V_{\text{coul}}(\mathbf{r}) + V_{\text{xc}}(\mathbf{r})\right)\phi_i(\mathbf{r}) = \varepsilon_i\phi_i(\mathbf{r})$$

Exchange-Correlation Functionals:

- Semi-local Functional: Perdew–Burke–Ernzerhof (PBE)

$$E_{xc} = \int n(\vec{r}) f(n_\uparrow, n_\downarrow, \nabla n_\uparrow, \nabla n_\downarrow) d\vec{r}$$

Fig.1: The Perdew-Burke-Ernzerhof exchange-correlation function is used in Kohn-Sham equation in this study. The calculated WS_2 band structure is closed to experiment results with and reasonable time cost.

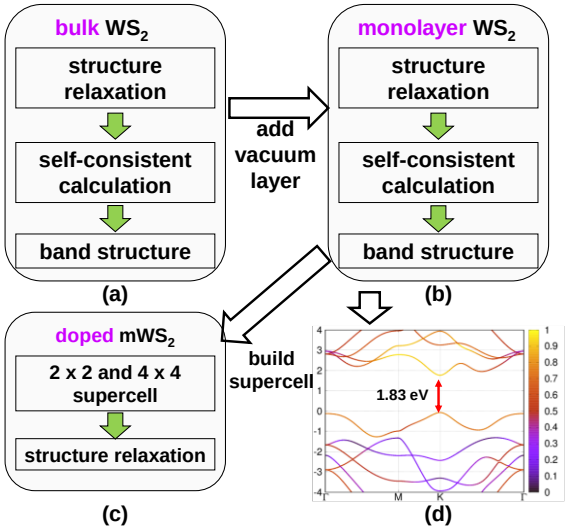

Fig.2: The simulation flow from (a) bulk WS_2 to (c) doped monolayer WS_2. (d) The obtained monolayer WS_2 band structure. The color bars indicate the weighting of band dominated by tungsten atoms. The direct bandgap is 1.83 eV for monolayer WS_2.

Formation energy:

$$E_{form} = E_{doped-mWS2} - E_{mWS2} + \sum n_i \mu_i$$

Fig.3: Specifically, $E_{Doped-mWS2}$ and E_{mWS2} are the total energies of the doped mWS_2 system and the pristine mWS_2, where n_i and μ_i are the number of atom i added (-1) or removed (+1) and the corresponding chemical potential, respectively.

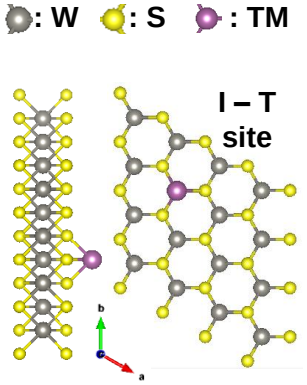

Fig.4: The most stable doped structure of mWS_2 of four possible doping sites is I-T site, the gray, yellow, and brown atoms are W, S, and doping transition metal, respectively. Two interstitial (I-) and two substitutional (S-) sites are simulated to determine the most stable site with lowest formation energy.

Table I: The formation energies (eV) of four doping sites for 4 × 4 mWS_2 supercell.

E_{form} (eV)	I – H	I – T	S – S	S – W
Sc	-1.735	**-1.855**	1.708	4.806
Ti	-1.656	**-2.245**	1.149	2.620
V	-3.664	**-4.138**	0.302	0.879
Cr	-0.685	**-0.851**	3.673	4.902
Mn	-0.487	**-0.728**	2.986	6.236
Fe	-1.158	**-2.139**	2.336	6.124
Co	-2.170	**-2.713**	2.115	6.667
Ni	-2.670	**-3.202**	1.713	7.722
Cu	-1.051	**-1.092**	3.381	10.177
Zn	-0.033	**-0.036**	5.949	12.437

Table II: The total magnetic moments (Mag. Mom.) of doped monolayer WS_2 supercell (SC.) with different doping concentrations.

Mag. Mom.	*Sc*	*Ti*	*V*	*Cr*	*Mn*
4 x 4 SC.	*3*	*4*	*5*	*6*	*5*
2 x 2 SC.	*1.15*	*4*	*5*	*5.62*	*4.62*
Mag. Mom.	***Fe***	***Co***	***Ni***	***Cu***	***Zn***
4 x 4 SC.	*2*	*1*	*0*	*1*	*0*
2 x 2 SC.	*2*	*1*	*0*	*0.11*	*0*

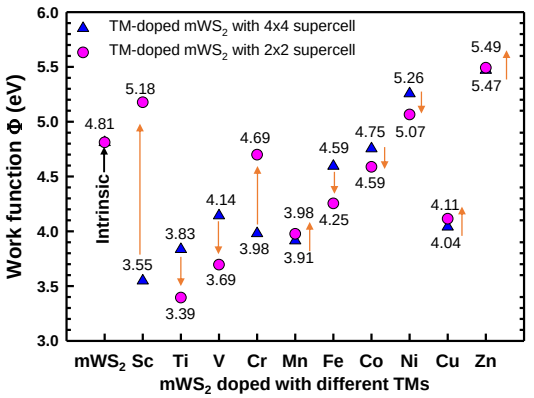

Fig.5: The work function of TM-doped mWS_2 with respect to different TM materials. The triangle and circle symbols are results of 4 × 4 and 2 × 2 supercells, respectively. The most stable structure, I-T, is simulated with two different doping concentrations. The arrows indicate how the work function changes as the doping concentration increases.

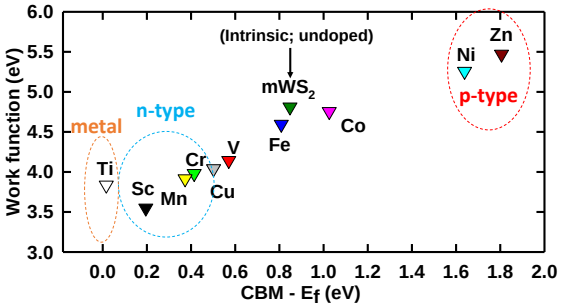

Fig.6: The work function versus the energy difference between the conduction band minimum (CBM) and the fermi level (E_f) of the TM-doped mWS_2