Monolayer Tungsten Disulfide with Transition Metal Doping

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

In this work, monolayer tungsten disulfide (mWS\textsubscript{2}) doped by various 3d transition metals (TM), with two different concentrations, $7.13 \times 10^{13}$ and $2.85 \times 10^{14}$ cm\textsuperscript{-2}, are studied by density-functional-theory simulation. Not like many studies assuming substitutional doping sites [1\textendash]2], we considered two interstitial (I\textsuperscript{−}) and two substitutional (S\textsuperscript{−}) 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) \cite{Perdew} 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 \cite{Y.-C. Tsai, Y.-C. Tsai}, 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\textsuperscript{0}; 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\textsubscript{2} are verified with experimental results. To determine the most stable site with lowest formation energy, four possible doping sites, two interstitial (I\textsuperscript{−}) and two substitutional (S\textsuperscript{−}) sites, are discussed. The formation energy is determined with the formula in Fig. 3. The interstitial site, I\textsuperscript{−}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\textsubscript{2} with respect to two concentrations. The titanium (Ti)-doped mWS\textsubscript{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\textsubscript{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.

**Acknowledgement:** This work was supported in part by the Ministry of Science and Technology (MOST), Taiwan, under grants MOST 106-2221-E-009-149, MOST 106-2622-8-009-013-TM, 107-2622-8-009-011-TM, 107-2221-E-009-094, and MOST 107-3017-F-009-001, and the “Center for mmWave Smart Radar Systems and Technologies” under the Featured Areas Research Center Program within the framework of the Higher Education Sprout Project by the Ministry of Education (MOE) in Taiwan.

**References:**

Kohn-Sham Equation:
\[ \left( \frac{\hbar^2}{2m} + V_{\text{ext}}(r) + V_{\text{ion}}(r) + V_{\text{corr}}(r) \right) \psi_i(r) = \varepsilon_i \psi_i(r) \]

Exchange-Correlation Functionals:
- Semi-local Functional: Perdew–Burke–Ernzerhof (PBE)
  \[ E_{xc} = \int n(r) f(n_{p}, n_{d}, V_{p}, V_{d}) d\mathbf{r} \]

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 reasonable time cost.

Formation energy:
\[ E_{\text{form}} = E_{\text{doped-}m\text{WS}_2} - E_{\text{mWS}_2} + \sum \mu_i n_i \]

Fig. 3: Specifically, \( E_{\text{doped-mWS}_2} \) and \( E_{\text{mWS}_2} \) are the total energies of the doped \( m\text{WS}_2 \) system and the pristine \( m\text{WS}_2 \) where \( n_i \) and \( \mu_i \) 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 \( m\text{WS}_2 \) 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 \( m\text{WS}_2 \) supercell.

<table>
<thead>
<tr>
<th>TM</th>
<th>Sc</th>
<th>Ti</th>
<th>V</th>
<th>Cr</th>
<th>Mn</th>
<th>Fe</th>
<th>Co</th>
<th>Ni</th>
<th>Cu</th>
<th>Zn</th>
</tr>
</thead>
<tbody>
<tr>
<td>I-T</td>
<td>-1.735</td>
<td>-1.855</td>
<td>1.708</td>
<td>4.806</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>S-S</td>
<td>-1.656</td>
<td>-2.245</td>
<td>1.149</td>
<td>2.620</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>S-W</td>
<td>-3.664</td>
<td>-4.138</td>
<td>0.302</td>
<td>0.879</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>S-W</td>
<td>-0.685</td>
<td>-0.851</td>
<td>3.673</td>
<td>4.902</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Fig. 5: The work function of TM-doped \( m\text{WS}_2 \) with respect to different TM materials. The triangle and circle symbols are results of \( 4 \times 4 \) and \( 2 \times 2 \) 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.