# Effect of Vacancy Defects and Strain on the Electronic Properties of Monolayer $MoS_2$

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**Abstract.** The electronic properties of the $MoS_2$ system under five different types of defects and biaxial compressive strain were investigated using first-principles calculations based on density functional theory (DFT). The results revealed that introduction of the defect transformed the $MoS_2$ system from direct band gap semiconductor to indirect band gap semiconductor. Among the five investigated defects, $V_s$ vacancy defect exhibited the lowest formation energy. When biaxial compressive strain was applied to pristine and defective $MoS_2$ systems, the band gap decreased with increasing strain. Especially, the $V_{Mo}$ vacancy defect system underwent a semiconductor to metal transition at approximately 6% compressive strain. This study provides theoretical insights into defect engineering and strain modulation strategies for optimizing the electronic properties of transition metal dichalcogenides.

**Keywords:** electronic properties; vacancy; biaxial strain.

## 1. Introduction

2D materials have attracted much attention in the field of nanoscience and technology due to their unique physical and chemical properties. In particular, transition metal dichalcogenides (TMDCs), such as $MoS_2$, $WS_2$, $MoTe_2$, $WTe_2$, etc., have become the focus of advanced materials research due to their layered structure and excellent electronic and optical properties [1-6]. The bulk material $MoS_2$ is an indirect bandgap semiconductor, while the monolayer $MoS_2$ is a direct bandgap semiconductor with a band gap of about 1.8 eV, which makes it show great application potential in the field of optoelectronics [7]. Defects and stress are two key factors influencing the properties of materials. Defects, such as vacancies, dislocations, etc., can change the electronic structure and conductivity of $MoS_2$, which can affect its application in electronic and optoelectronic devices.

In recent years, researchers have identified and characterized defects in $MoS_2$ by means of electron microscopy, Raman spectroscopy, etc. Researchers explored the formation process and mechanism of defects through theoretical and experimental studies [8-14]. The research team of Wang et al. systematically studied the effect of different sulfur vacancy concentration and distribution on the performance of $MoS_2$ based hydrogen evolution reaction (HER) catalyst by means of high throughput calculation, and realized efficient hydrogen evolution [8]. Zhou et al. systematically revealed the intrinsic structural defects in monolayer $MoS_2$ grown by chemical vapor deposition, and uncovered a new edge reconstruction mode that exists as a transition state during the material growth process [9]. Lei et al. revealed that the electronic distribution around vacancy defects exhibits obvious localization characteristics according to the first-principles calculations based on density functional theory. The sulfur vacancy is found to be more readily formed than the molybdenum vacancy [12].These studies not only reveal the effect of defects on the properties of MoS2, but also provide the possibility for the repair and optimization of defects. However, there are still challenges in precisely controlling the types of defects, understanding the mechanisms by defects affect and using defects to improve material properties. Stress, as an external disturbance, can cause the change of crystal structure, which leads to the change of band structure and further affects the electronic properties of materials [15-21]. Li et al. found that tensile strain significantly changed the band gap through density functional theory calculations [16]. Lloyd et al. demonstrated continuous and reversible tuning of the optical band gap of a suspended monolayer $MoS_2$ film up to 500 meV by applying a very large biaxial strain [17]. Nechiyil et al. studied the effect of strain on the electrical properties of single-layer $MoS_2$, emphasizing the pivotal role played by defects [18].

Therefore, a deep understanding of the effects of defects and stresses on the properties of $MoS_2$ is essential for optimizing material properties and developing new applications.

This work is to investigate the effects of defects and stresses on the electronic structure and physical properties of $MoS_2$, as well as the potential implications of these effects for $MoS_2$ applications in electronics, optoelectronics, and energy-related fields. By means of an deeply analysis, we hope to provid theoretical support and experimental guidance for optimizing the performance of $MoS_2$ materials and exploring novel application.

## 2. Calculations

The Quantum Espresso (QE) software package based on density functional theory was used in this work [22, 23]. The electron exchange-correlation energy is calculated using the generalized gradient approximation (GGA) by Perdew, Burke, and Ernzerhof (PBE) [24]. The convergence test was carried out before the structure optimization. The cutoff energy for the plane-wave basis was 60 Ry. The k-point mesh in Brillouin zone uses 4 × 4 × 1 for the geometry optimization and 10 × 10 × 1 for the density of state. In order to avoid the interlayer interaction due to periodic calculation method, the vacuum layer was added to be more than 10 Å.

The stress is applied to the $MoS_2$ system by changing the lattice constant. The strain produced when the stress is applied is

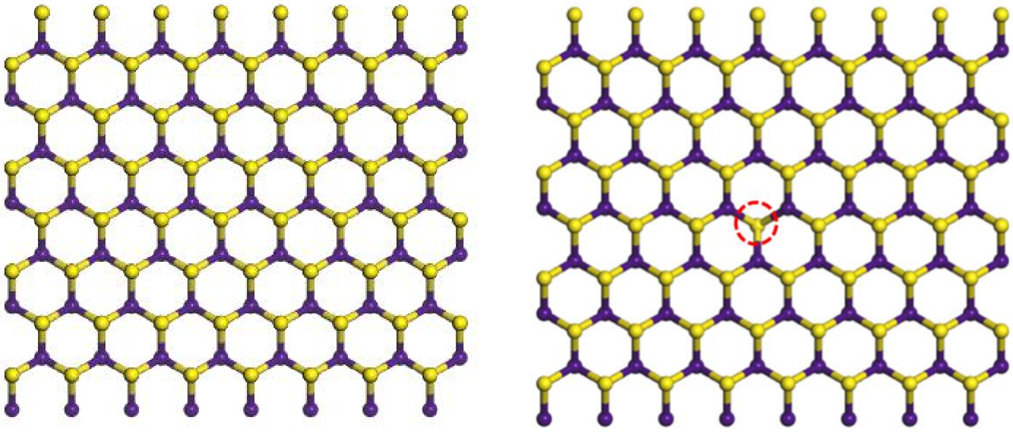
$$\varepsilon = \frac{\Delta a}{a}$$

In the above formula, $a$ represents the lattice constant when the stress is not applied, and $\Delta a$ represents the difference between the lattice constant when the stress is applied and when the stress is not applied.

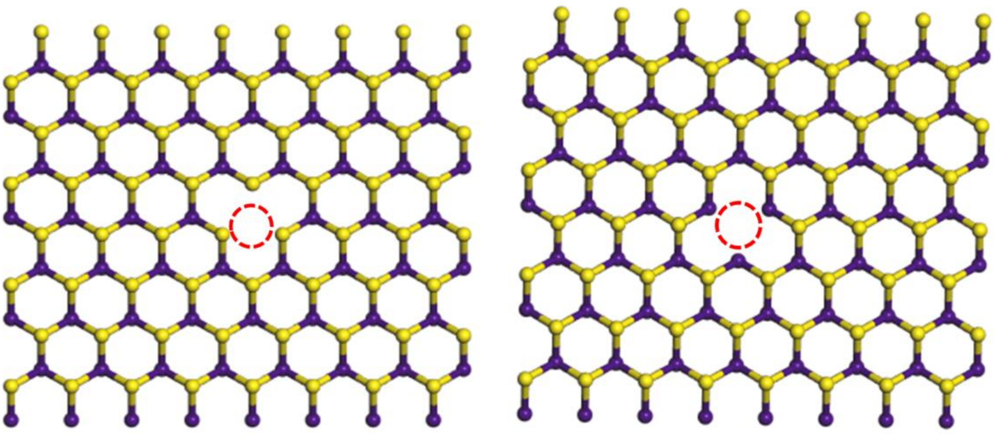
## 3. Results and Discussions

### 3.1 The strucures of pristine and detective $MoS_2$

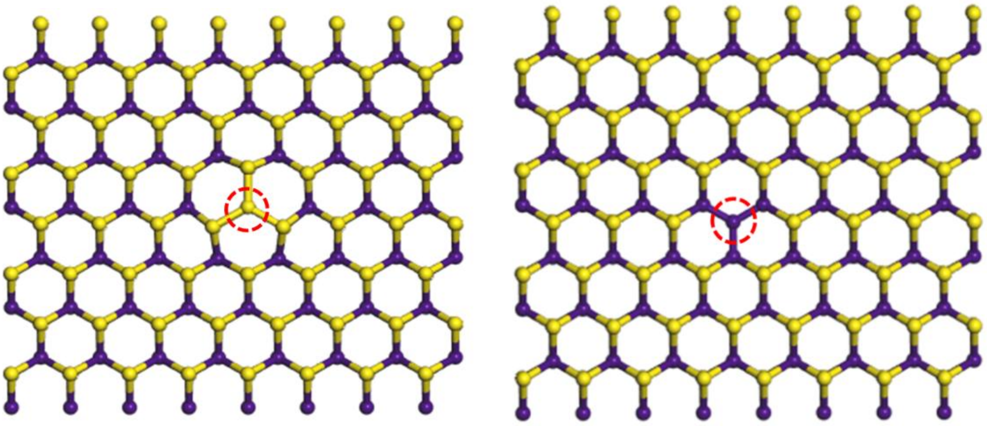
We take a rectangular primitive cell with one Mo atom and two S atoms and build 8x8x1 supercell with 64 Mo atoms and 128 S atoms as pristine $MoS_2$ system, as shown in Fig. 1(a). The following five defect types are investigated. They are S vacancy (S atom monovacancy, Vs), Mo vacancy (Mo atom monovacancy, $V_{Mo}$), $S_2$ vacancy (S atom divacancy, $V_{S_2}$), $MoS_2$ antisite defect (two S atoms replacing Mo atom, $V_{MoS_2}$) and $S_2Mo$ antisite defect (Mo atom replacing two S atoms, $V_{S_2Mo}$) , as shown in Fig. 1(b)-(f).



(a) $MoS_2$ (b) $MoS_2$_$V_s$



(c) $MoS_2$_$V_{Mo}$ (d) $MoS_2$_$V_{S_2}$



(e) $MoS_2$_$V_{MoS_2}$ (f) $MoS_2$_$V_{S_2Mo}$

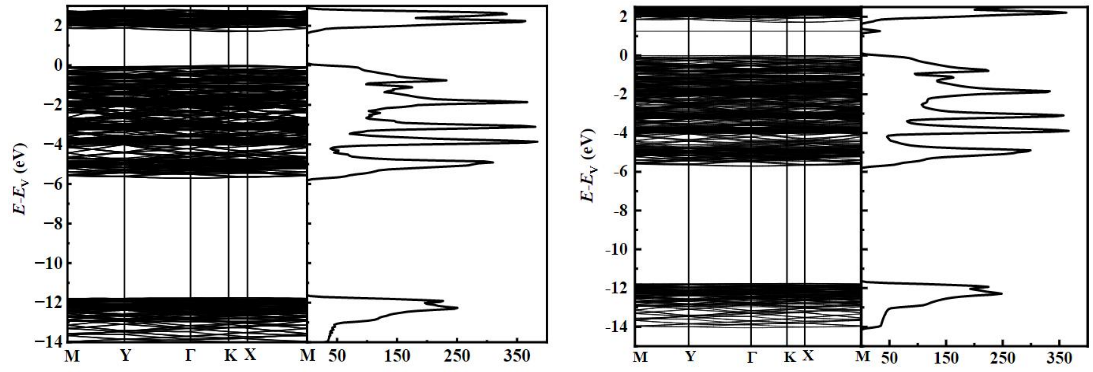
Fig. 1 The structures of pristine $MoS_2$ and detective $MoS_2$

### 3.2 The band strucures and density of states

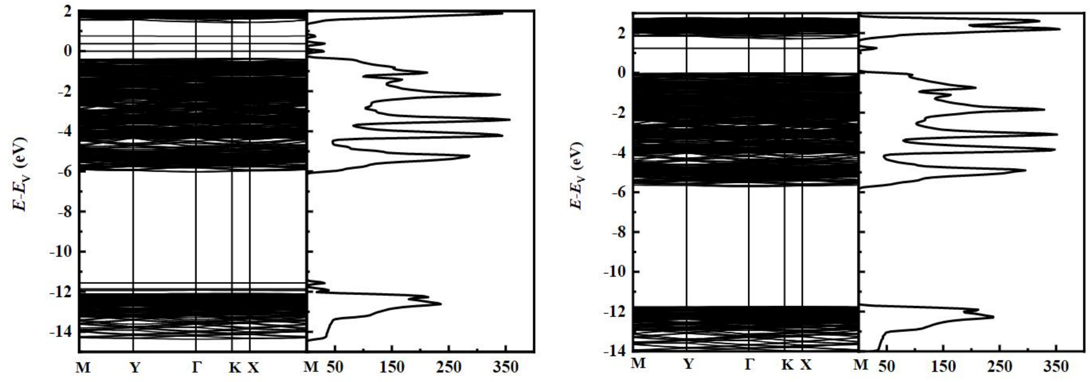
When there are impurities or defects in the semiconductor, the bound state corresponding to the energy band is formed. Bound electrons form impurity levels, which exist in the band gap of the semiconductor and play a decisive role in the properties of the actual semiconductor.

Through the calculation of band structure and density of state, we obtain the electronic structure of $MoS_2$ systems as shown in Fig. 2(a). It can be seen that $MoS_2$ is a direct band gap semiconductor and the band gap is 1.71 eV.

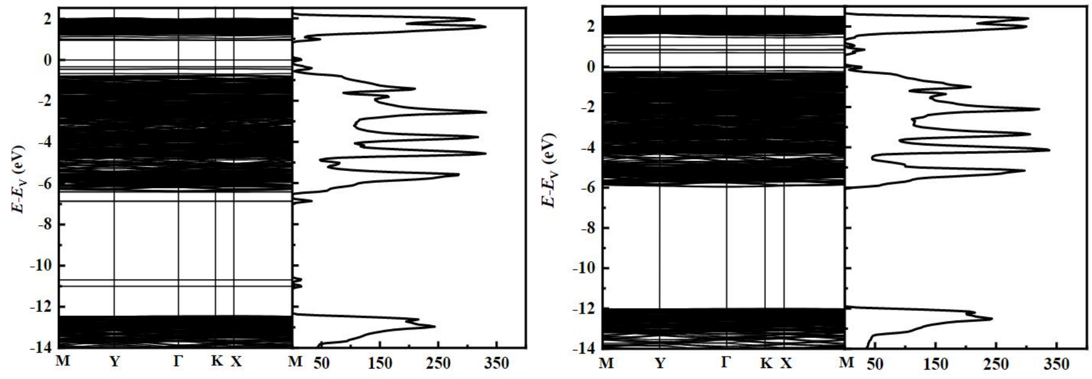
Compared with the pristine $MoS_2$, different number of new energy levels have appeared in energy band structures, is shown in Fig. 2 (b)-(f). The valence band top (VBM) moves down slightly, and the defect energy level is introduced near the conduction band bottom (CBM) in the forbidden band, resulting in a decrease in the band gap width, which is 1.26eV (double degenerate) above the valence band top for $V_S$ vacancy system. $V_{Mo}$ vacancy system produce defect levels near the valence band top, two at 0.36eV above the valence band top (double degenerate), and one at 0.75eV. The $V_{S_2}$ vacancy system is similar to the S vacancy system and there is a defect level at 1.23eV (double degenerate) above the top of the valence band. $V_{S_2Mo}$ vacancy system introduce defect states in the band gap, which are located above the valence band top by 0.69eV, 0.85eV (double degenerate), and 1.06eV. The $V_{MoS_2}$ vacancy system introduces a defect state in the band gap, 0.96eV (double degeneracy) above the top of the valence band. From the analysis of density of state, it can be found that vacancy defects have little effect on valence band energy distribution. The small peak in the band gap region corresponds to the defect energy level introduced by the defect.



(a) $MoS_2$ (b) $MoS_2\_V_s$



(c) $MoS_2\_V_{Mo}$ (d) $MoS_2\_V_{S_2}$



(e) $MoS_2\_V_{MoS_2}$ (f) $MoS_2\_V_{S_2Mo}$

Fig. 2 The band structure and density of states of pristine and detective $MoS_2$

### 3.3 The form energy of defective $MoS_2$ systems

The formation energy of vacancy defect in the pristine $MoS_2$ system is calculated as follows

$$E_f = E_{\mathrm{MoS_2\text{-}vac}} - E_{\mathrm{MoS_2}} + nE_x$$

Where $E_{\mathrm{MoS_2\text{-}vac}}$, $E_{\mathrm{MoS_2}}$ and $E_x$ represent the energy of $MoS_2$ with vacancy defects, the energy of pristine $MoS_2$, and the energy of the corresponding single vacancy atom, respectively. And $n$ is the number of vacancy atoms. By calculating the formation energy of several defect systems, as shown in Table 1. The formation energy of $V_S$ vacancy is the lowest, which is 3.63eV, indicating that $V_S$ vacancy is relatively easy to form. Secondly, the formation energy of $V_{MoS_2}$ vacancy and $V_{Mo}$ vacancy defects are low, which are 6.36eV and 6.99eV respectively. The formation energy of $V_{S_2}$ vacancy defect is about 2 times that of $V_S$ vacancy defect, which is 7.21eV. The formation energy of $V_{S_2Mo}$ vacancy defect is the largest about 12.84eV and is relatively difficult to form.

Table 1. The formation of different defective $MoS_2$ systems

| System | Formation Energy $E_f$ (eV) |
|---|---|
| $MoS_2$-$V_S$ | 3.63 |
| $MoS_2$-$V_{Mo}$ | 6.99 |
| $MoS_2$-$V_{S_2}$ | 7.21 |
| $MoS_2$-$V_{MoS_2}$ | 6.36 |
| $MoS_2$- $V_{S_2Mo}$ | 12.84 |

### 3.4 The band gap variation under strain

The properties of the material can be regulated and its application areas can be expanded by applying strain. Strain can effectively regulate the band structure of 2D transition metal sulfide TMDCs materials. We applied strain by changing the lattice parameters. The combined effect of biaxial compression strain and vacancy defects, can significantly change the electronic properties of $MoS_2$. And the lattice distortion, band reconstruction and charge redistribution of $MoS_2$ system can be achieved. The biaxial compression strain results in the contraction of monolay-layer $MoS_2$ lattice, shortening of Mo-S bond length, enhancement of covalent bond strength, and distortion of local lattice around defects. With the increase of strain, the band gap of pristine $MoS_2$ decreases gradually. When 10% biaxial compression strain is applied, the band gap drops to about 1.24 eV. When 5% biaxial compression stress is applied, the band gap of the S vacancy defect system decreases to about 1.31 eV, which can be used for near infrared detection. As the strain increases, the band gap of the Mo vacancy defect system and $MoS_2$ vacancy defect system decreases, and the semiconductor-to-metal transition occurs at biaxial compression strain of approximately 6% and 10%, respectively.

## 4. Summary

The pristine $MoS_2$ and defective $MoS_2$ systems were studied using first principles calculations. The electronic properties, vacancy effect and biaxial strain effect are investigated. The results show that pristine $MoS_2$ is a direct band gap semiconductor and the band gap is 1.71 eV. The vacancy defective $MoS_2$ becomes indirect band gap semiconductor and there are defective energy levels in energy band structures. The sulfur vacancy defect exhibited the lowest formation energy among the five investigated defects system and means $V_S$ vacancy is relatively easy to form in $MoS_2$ system. The band gap decreased with increasing biaxial compressive strain. Especially, the $V_{Mo}$ vacancy defect system underwent a semiconductor-to-metal transition at approximately 6% compressive strain. This study provides theoretical basis and experimental guidance and has great significance to optimize material properties and develop new applications for $MoS_2$ system.

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