Chalcogenide Letters Vol. 20, No. 6, June 2023, p. 409 - 421

Tensile deformation of S adsorbed in a monolayer of ReS_2 affects its electronic structure and optical properties

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Using density functional theory, the effect of biaxial tensile strain on adsorption of S in ReS_2 monolayer is calculated. The study finds intrinsic ReS_2 system and monolayer ReS_2 adsorbed S system are affected by tensile deformation. Intrinsic ReS_2 has direct band gap. As S appears, the system becomes indirect band gap. With tensile deformation amount of the intrinsic ReS_2 system reaching 10%, the band gap reduces to 0.064eV. The growth rate of reflection and absorption coefficient are decreased by tensile deformation. The maximum reflection and absorption peak undergo red shift, improving the light reflection and absorption ability of adsorption system.

(Received March 16, 2023; Accepted June 10, 2023)

Keywords: ReS_2, Tensile deformation, Electronic properties, Optical properties

1. Introduction

As graphene was prepared in 2004 by Geim's research group at the University of Manchester, UK [1], it has attracted the attention of many scientists, Graphene [2-4] has excellent electrical properties and unique optical properties, a wide range of ultrafast photonic applications can be achieved with this device, and graphene can sense the adsorption and separation of molecules through the change of local carrier concentration, and then be used to prepare various sensors [5]. However, as graphene has a zero band gap value, it is not suitable for semiconductor applications development. Transition metal dichalcogenides (TMDs), as a new type of graphene-like materials, generally have large band gaps and unparalleled properties in physics, chemistry and optoelectronics. With its potential to replace graphene in many fields such as photoelectric detection, catalysis, sensing, and energy storage, it holds great promise [6-11].

Among them, rhenium disulfide has attracted widespread attention. Rhenium disulfide is a semiconductor material with an approximately 1.5eV band gap in the direct band gap [12], the interlayer coupling force of ReS_2 is weak, with a thicker few-layer ReS_2, the state density is higher, and a higher ability to absorb light, potentially enabling it to detect weak signals with high responsiveness. Promising materials for sensitive optoelectronic applications [13]. However, it is impossible for ReS_2 to fabricate high-efficiency devices due to the low carrier mobility and

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https://doi.org/10.15251/CL.2023.206.409

non-magnetic behavior [14]. In order to further optimize the physical properties of ReS2, the researchers used doping, adsorption, defects and other modification methods to effectively control the electronic structure of ReS_2.

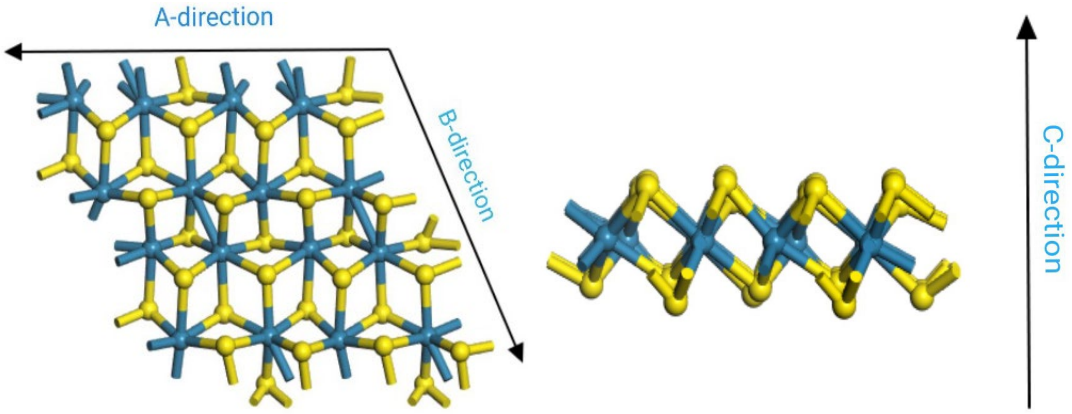
For example, Y. M. Min et al. regulated monolayer ReS2 and found that the s4-deficient ReS2 is the most stable, defect states are characterized by Re-d orbitals and S-p orbitals [15], Obodo et al. doped lanthanide atoms in monolayer ReS2, changing its electronic structure, introducing defect states in the energy gap and resulting in small changes to their overall density [16]. In addition, axial tension and compression and shear strain are also an important means to adjust the optoelectronic properties of materials. For example, He et al. performed shear deformation of O-adsorbed black phosphorene, generating the band gap transitions directly to indirectly[17], as part of a study by Liukailong, tensile strain was applied to monolayer MoS2 in order to examine its optoelectronic properties, and found that when the tensile strain is 10%, the forbidden band width of the material becomes 0, and the transition from semiconductor to metal is realized [18], Luo, M, et al. transform MoS2/ReS2 heterostructures from direct bandgap semiconductors to indirect bandgap semiconductors by compressive transformation [19].

Many metallic and non-metallic elements have been introduced in the existing studies on ReS2, however, there are only a few reports on the introduction of oxygen group elements for modification, meanwhile, deformation applied to ReS2 has also been studied as a conventional regulation method. Thus, in this paper, both adsorption and strain modulation methods were used to study ReS2, and the optical and electronic properties of the S atom-adsorbed monolayer ReS2 model under tensile strain were calculated, it is anticipated that this study will guide the use of monolayer ReS2 in optoelectronic devices.

2. Methods and models

Density functional theory (DFT) is used in all calculations in this paper, and are calculated using the CASTEP module in Material Studio software [20], a method to the plane wave pseudopotential using the generalized gradient approximation and the Perdew-Burke-Ernzerhof function (PBE) [21] based on different tensile deformations, the structure of the adsorbed S and intrinsic ReS2 systems was optimized and the total energy was calculated. In each model calculation, the plane wave cutoff energy is set to 450eV, and the Monkhorst-Pack grid is set to 5x5x1 [22], the convergence criterion of single-atom energy is 1.0×10^{-6}eV, and the convergence criterion of interatomic force is 0.01eV/Å. Using a vacuum layer with a thickness of 20 Å, the interlayer forces of each layer on the surface of ReS2 are avoided.

In this paper, a 2x2 single-layer ReS2 supercell is used for simulation. As shown in Figure 1, ReS2 unit cells contain 4 Re atoms and 8 S atoms, while supercells contain 16 Re atoms and 32 S atoms, with a total of 12 corresponding adsorption sites, as shown in Figure.2. In Figures 1 and 2, Re atoms are represented by blue spheres, and S atoms by yellow spheres. Calculation of the electronic structure of the S-absorbing system under biaxial tensile strain, by simultaneously adjusting the lattice parameters in directions A and B, tensile deformation can be achieved, the calculation deformation formula is defined as $\varepsilon = (L - L_0) / L_0$,among them, L_0 is the lattice parameter before stretching,and L is the lattice parameter after stretching.



(a) *(b)*

Fig. 1. Single-layer ReS2 model (a)Top view of single-layer ReS2 (b) Side view of single-layer ReS2.

At the same time, in order to study the structural stability of the monolayer ReS2 adsorbed S atom system under different stretching variables, the adsorption energy is defined as follows:

$$Eads=Etotal-Eintrinsic-Eadatom \quad [26]$$

The energy of the intrinsic ReS2 is denoted by *Eintrinsic*, the energy of the adsorption system is denoted by *Eadsorption*, the energy of the adsorbed single atom is denoted by *Eadatom*. An adsorption process that is endothermic has a positive adsorption energy according to the definition of adsorption energy; when the adsorption energy is negative, the surface adsorption process is exothermic, and an adsorption energy with a higher absolute value indicates a more stable structure.

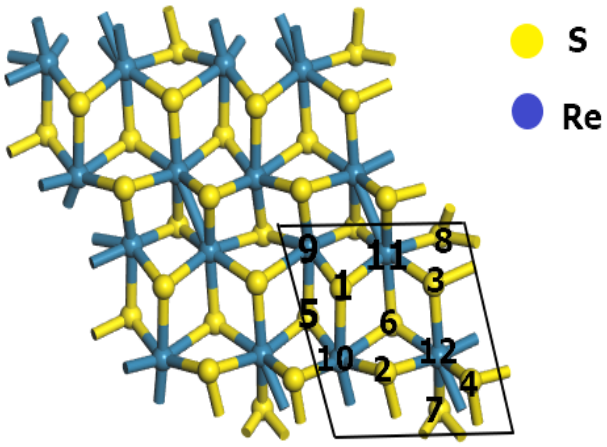


Fig. 2. Monolayer ReS2 adsorption site,ReS2 primitive cells are in the black box

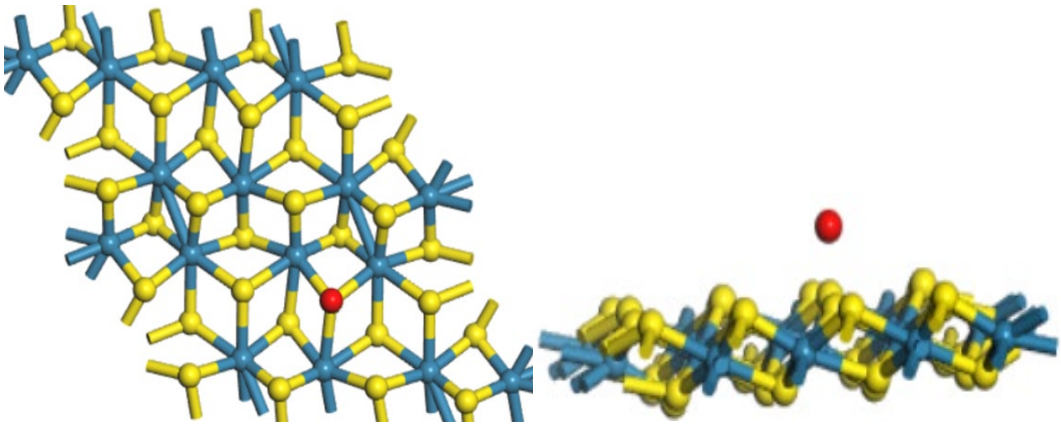
3. Results and discussion

3.1. Structural optimization and stability

Before calculating the adsorption system and subsequent tensile deformation, we optimized the unit cell of ReS2. The optimized intrinsic ReS2 lattice parameters a is 6.40 Å and b is 6.50 Å, it is not much different from the experimental value of ReS2 where a is 6.42 Å and b is 6.52 Å [12], the calculated bond lengths of Re-S are 2.32 Å, 2.36 Å, 2.38 Å, 2.42 Å, 2.46 Å, 2.52 Å, which are the same as 2.33A˚, 2.37A˚, 2.39A˚, 2.42A˚2.47A˚, 2.52A˚ in literature [23], basing on the results of this study, the model and parameters selected are reliable. The selection of coverage refers to reference [14], we have optimized the adsorption sites of S atoms on the intrinsic monolayer ReS2. The adsorption energies for all adsorption points are shown in Table 1. It is found that the adsorption architecture of site 1 is the most stable, which is consistent with the calculation results in [23]. The following calculations will be based on site 1.

Table 1. Adsorption energies of adsorbed S atoms at each site of intrinsic monolayer ReS2.

site	1	2	3	4	5	6
Energy /ev	-3.11	-3.03	-3.06	-2.91	-1.45	-3.06
site	7	8	9	10	11	12
Energy /ev	-3.03	-2.91	-1.76	-1.67	-1.74	-1.68



(a) *(b)*

Fig. 3. The optimized geometry of monolayer ReS2 adsorbed S atoms (a) top view (b) side view.

The adsorption energies of the monolayer ReS2 adsorption S atom system under varying degrees of tensile deformation are shown in Table 2. As the stretching type variable increases from 0% to 10%,in the current variable range, the absolute value of adsorption energy shows an increasing trend, and greatly enhances the structural stability; when the tensile variable increases from 0% to 8%, although the absolute value of adsorption energy increases slightly, the overall change is weak. It only increases from 3.16eV to 3.33eV, when the shape variable increases from 8% to 10%, the adsorption energy value increases by 1.81eV, indicating that when the deformation

amount is 0%-8%, the structure is more affected by the tensile deformation. When the shape variable is greater than 8%, the structure is greatly affected by tensile deformation.

Table 2. Adsorption energies of monolayer ReS2-adsorbed S atoms system under different degrees of tensile deformation.

strain	0%	2%	4%	6%	8%	10%
Energy/eV	−3. 16	−3. 18	−3. 18	−3. 31	−3. 33	−5. 13

3.2. Electronic structure of monolayer ReS2 adsorbed S subjected to tensile deformation

ReS2 is a direct gap semiconductor with the top of the valence band and the bottom of the conduction band originating from the d-orbital of the Re atom and the p-orbital of the S atom[24]. The minimum energy required for an electron in the valence band of a semiconductor to be excited to jump to the conduction band to produce a carrier is represented by the size of the band gap. The larger the band gap, the harder it is for electrons to be excited from the valence band to the conduction band, the lower the intrinsic carrier concentration, and the lower the conductivity [25-26]. We have calculated the energy band structures of intrinsic ReS2 and monolayer ReS2 adsorbed S atoms. Among them, the band gap of the intrinsic monolayer ReS2 is 1.446 eV,it is almost consistent with 1.43 based on the reference [10], its energy band structure is shown in Figure 4(a), and Figure 4(b) is the energy band structure of the single-layer ReS2 adsorption S atom system. In Fig. 4(a), the intrinsic single-layer ReS2 electron system is a direct bandgap semiconductor structure, and the top of the valence band and the bottom of the guide band appear simultaneously at the G point, while in Fig. 4(b), the monolayer ReS2 electron system shows indirect bandgap semiconductor structural properties after adsorption of S atoms, with a slight decrease in bandgap value of 0.087eV as the valence band tops off at the K point. In Fig. 4(c), the black line is the DOS curve of the intrinsic ReS2, and the red line is the DOS curve of the S atom adsorbed by ReS2, corresponding to the respective energy band structure diagrams（Due to the large cross-sectional range of energy values for the density of states of the system, energy values of -20eV to 8eV have been chosen for analysis in the graphs for ease of observation）. As can be seen from the figure, with the introduction of the S atom, the ReS2 adsorption system introduces impurity bands, and the corresponding density of states curve appears two new wavelet summits at -15.4eV and -10.4eV.

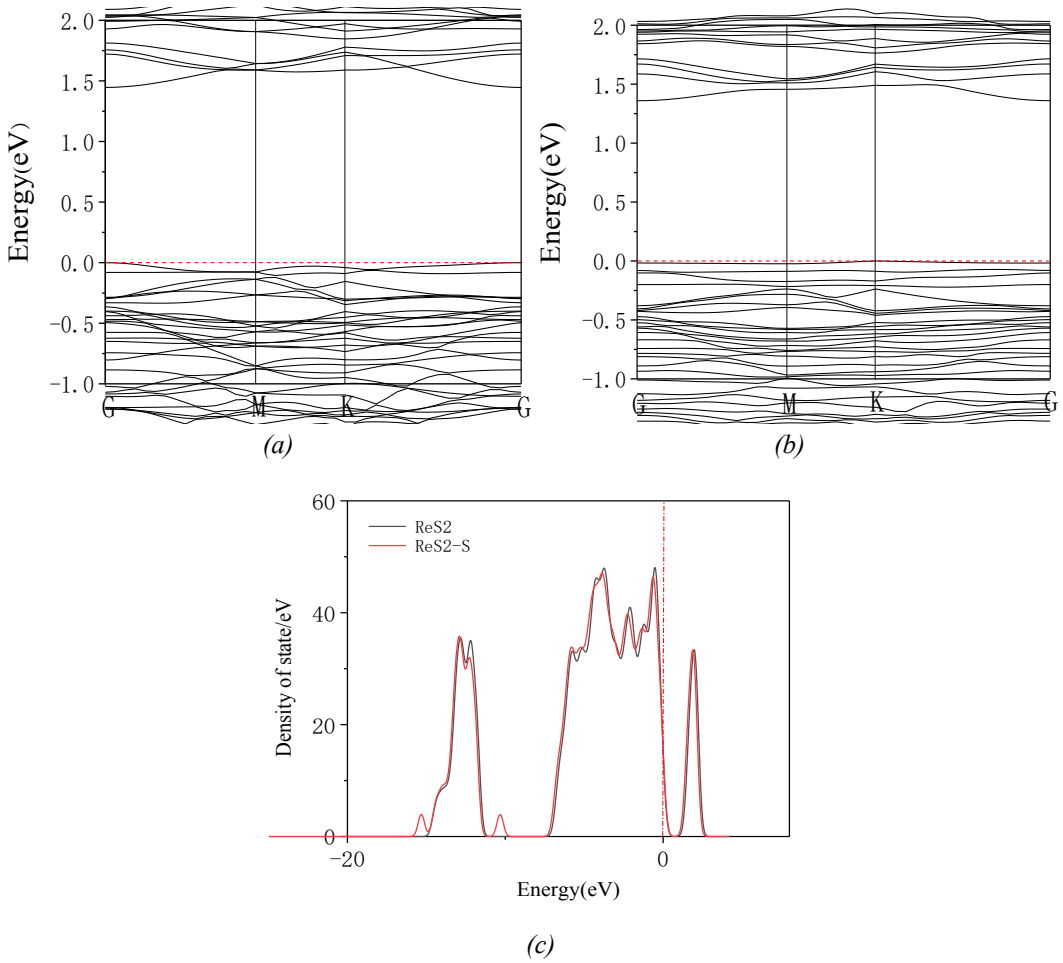


Fig. 4. (a) intrinsic ReS2; (b) ReS2 adsorbs S atoms; (c) Intrinsic ReS2 and the density of states of the adsorption system

The energy band structure of the ReS2 adsorbed S-atom system at 0%-10% stretching deformation is given in Figure 5. The red dashed line indicates the Fermi level. Further, in order to analyse the impact of tensile deformation on the band gap of the adsorbed systems, the band gap values for the monolayer ReS2 and ReS2 adsorbed S-atom systems at different tensile deformations are presented in Table 3 respectively. And Fig. 5(g) shows the correlation curve between the tensile deformation amount and the band gap value of the monolayer ReS2 and ReS2 adsorbed S atom system.Under the tensile effect of intrinsic ReS2, as the tensile deformation rises from 0% to 2%, the band gap value declines from 1.446eV to 1.363eV; as the tensile deformation amount is 4%, the band gap value declines to 1.225eV; as the tensile deformation amount is 6%, the band gap value is 1.005eV; as the tensile deformation amount is 8%, the band gap value is 0.788eV; as the tensile deformation amount reaches 10%, the band gap of its energy band structure is The gap value plummeted to 0.064eV. The band gap value of the S-atom system introduced by ReS2 declines with rising tensile deformation. When the stretching amount increases from 0% to 2%, the band gap value decreases from 1.359 eV to 1.249 eV; the stretching amount increases to 4% , the band gap value declined to 1.139eV; when the stretching amount increased to 6%, the band gap value declined to 1.002 eV; when the stretching amount was 8%, the band gap value was

0.822 eV, and when the stretching amount was 10% , the band gap value is reduced to 0.437eV. It has been proved that from the above results that within the research scope, the tensile deformation will continuously reduce the energy gap of the two systems of intrinsic ReS2 and ReS2 adsorbed S atoms. The reduction of the gap value becomes more and more severe, and the descending curve changes from gentle to steep. The intrinsic ReS2 electronic system is relatively more sensitive to tensile deformation. When the stretching amount reaches 10%, the property of the structural system is transformed from an indirect bandgap semiconductor structure to a metallic structure. Both systems are indirect bandgap semiconductor structures during tensile deformation.

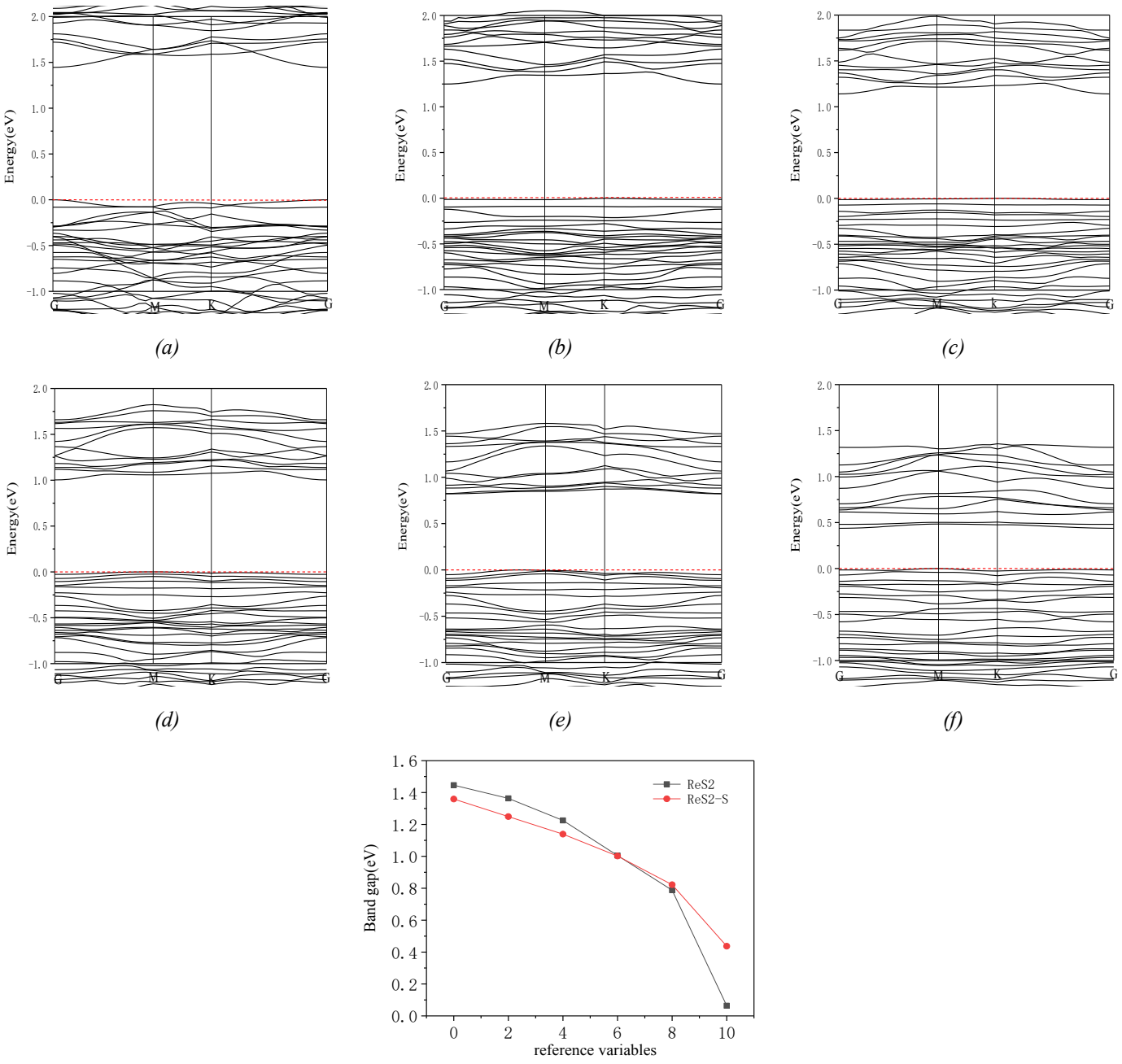


Fig. 5. (a)~(f) Band structures of ReS2-adsorbed S atom systems with stretches of 0%, 2%, 4%, 6%, 8%, and 10%;(g) Curves of intrinsic ReS2 and ReS2-adsorbed S systems as a function of stretching amount.

Table 3. Band gap values of intrinsic monolayer ReS2 and monolayer ReS2 adsorbed S atoms under different tensile deformations.

stretch deformation	0%	2%	4%	6%	8%	10%
eigenvalues /eV	1.446	1.363	1.225	1.005	0.788	0.064
Sorption values /eV	1.359	1.249	1.139	1.002	0.822	0.437

As we can seen from the data in Table 3 that during the course of raising the tensile deformation amount from 0% to 6%, the band gap value of the intrinsic ReS2 is always larger than that of the ReS2 adsorbed S atom system, and the tensile deformation amount increases from 8% to 10%. In the process of increasing the tensile deformation from 8% to 10%, the intrinsic ReS2 band gap value becomes smaller than that of the ReS2-adsorbed S atom system. In general, the band gap value of the monolayer ReS2 adsorbed S atom system will continue to decrease as tensile deformation increases, and then its conductivity will continue to increase.

The density of states for ReS2 adsorbed S atoms with different stretching deformation variables is given in Figure 6. From Figure 6(a), as we can seen that the density of states of intrinsic ReS2 is determined by the s-state electrons, p-state electrons and the d-state electrons of Re atom and the s and p-state electrons of the S atom are composed of many density-of-state summits in the valence band, and the peaks around -80eV are all contributed by the s-state electrons of the Re atom; the largest summit appears from -43eV to -41eV, its energy value originates almost entirely from the p-state electrons of the Re atom, while the p-state electrons of the S atom play a very small role; the summits from -15eV to -11eV are mainly derived from the s-state electrons of S atoms, the s, p and d state electrons of the Re atom and the p state electrons of the S atom play a negligible role; the summit from -7eV to 0eV is mainly contributed by the d-state electrons of the Re atom and the p-state electrons of the S atom; in the conduction band part, there is only one summit with an energy value of about 0eV-3eV, which is jointly contributed by the d-state electrons of the Re atom and the p-state electrons of the S atom. As we can seen from Figure 6(b)-(g) that after ReS2 adsorbs S atoms, all models of the adsorption system have higher density of states summits in the conduction band part and the valence band part than the intrinsic model, and the energy value is about two small density of states summits appear at -15eV and -10eV positions, almost all of which are derived from the s-state electrons of S atoms. With the enhancement of the tensile deformation amount, at the energy value of about -4 eV, the role of the s-state electrons of the S atom gradually increases, the corresponding summit density of states keeps increasing, and the summit density of states on the right side of the Fermi level is 0 gradually approaching the Fermi level，as the tensile deformation amount enhances from 8% to 10%, the summit density of states at this position gradually increases from 0 due to the rule of the d-state electrons of the Re atom and the p-state electrons of the S atom.

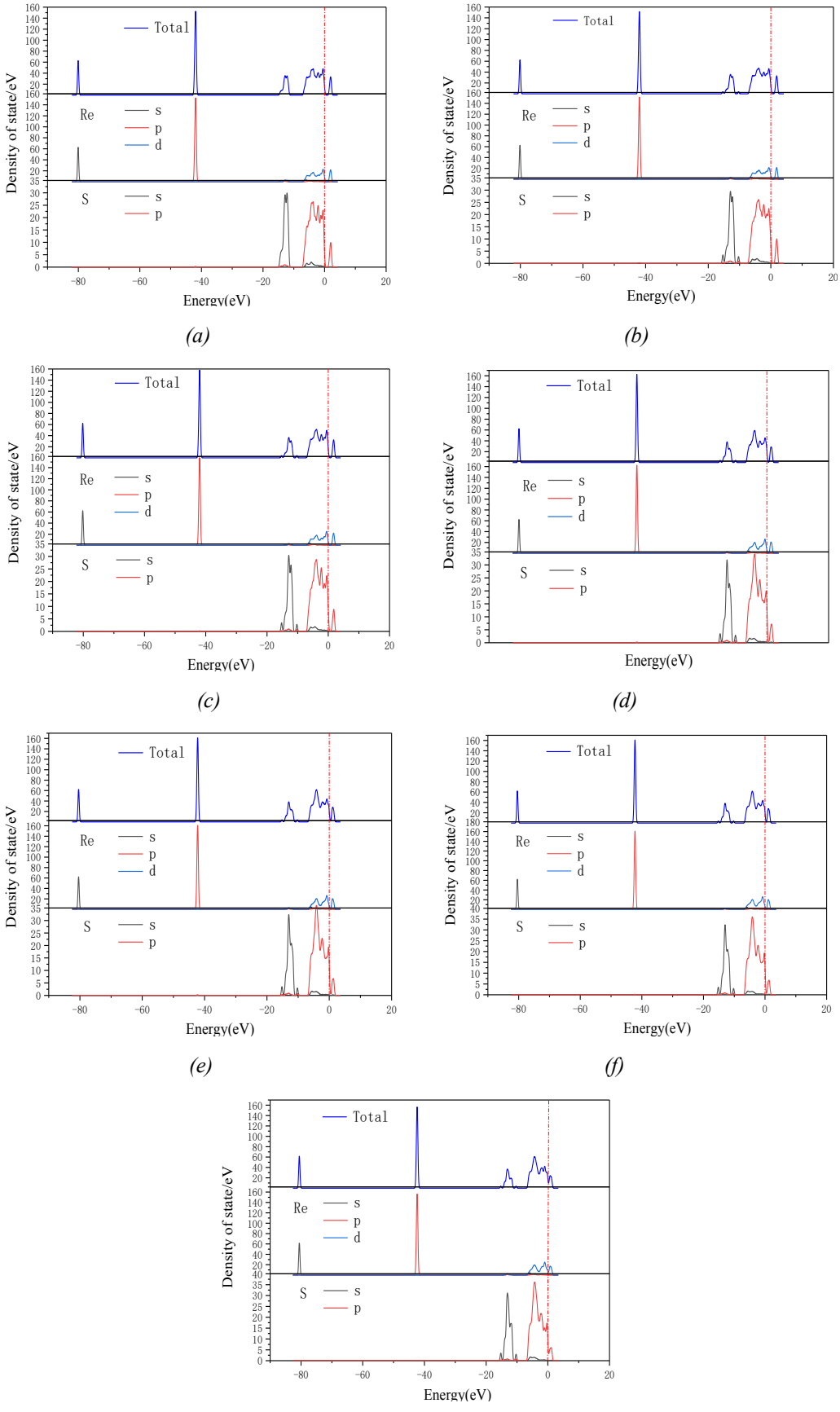


Fig. 6. (a)Density of states of intrinsic ReS2; (b)-(g) Density of states of ReS2-adsorbed S atom system with stretching amount of 0%-10%.

3.3. Effects of tensile deformation on optical properties of adsorbed S in monolayer ReS2

In order to investigate the optical properties of monolayer ReS2 adsorbed S-atom systems as affected by tensile deformation, the reflectance and light absorption coefficient of the system were calculated and analyzed from these two aspects, as shown in Fig. 7. It can be seen from Figure 7(a) to(c) that all the adsorption systems start to reflect light at a wavelength of about 15 nm, and the rate of increase in reflectance decreases with increasing tensile deformation, and at a wavelength of about 28 nm. The first small reflection summit occurs at the wavelength of 210 nm, the second reflection summit occurs successively at 210 nm, and the third reflection summit occurs successively at the wavelength of about 425 nm. At the second reflection summit, the summit value of the reflection summit of the adsorption system first rises and then falls as the tensile deformation increases. When the tensile deformation amount is 6%, the peak-to-peak value of the reflection is the largest, which is about 44892. At the third reflection summit, the reflection summit value of the adsorption system decreases in turn according to the tensile deformation amount of 8%, 4%, 6%, 2%, 0%, and 10%. The reflectivity of the adsorption system is red-shifted as the amount of tensile deformation increases. At a wavelength of about 6941 nm, all adsorption systems stopped reflecting light, and the larger the amount of tensile deformation, the larger the reflection range.

As we can seen from Figure 7(d) to (f) that all adsorption systems start absorbing light at a wavelength of around 27 nm, and the growth rate of the absorption coefficient decreases with the increase of the tensile deformation of the adsorption system. The first absorption summit occurs at about 28nm, a small reflection summit occurs at the wavelengths of about 90nm and 110nm, the third absorption summit occurs at the wavelength of about 200nm, and the fourth absorption summit occurs at the wavelength of about 400nm, observing these absorption summits, it's not hard to find that the light absorption coefficient of the adsorption system decreases with the enhancement of the tensile deformation amount. With higher tensile deformation, the highest absorption summit of the adsorption system is red-shifted and the degree of red-shift increases with the amount of stretching and deformation of the system. In addition, all adsorption systems stopped absorbing light at the wavelength of 6942 nm, and the greater the tensile deformation, the wider the absorption range of the corresponding adsorption system. It can be seen from the above analysis that the tensile deformation improves the light reflection and absorption ability of the ReS2-adsorbed S atom system.

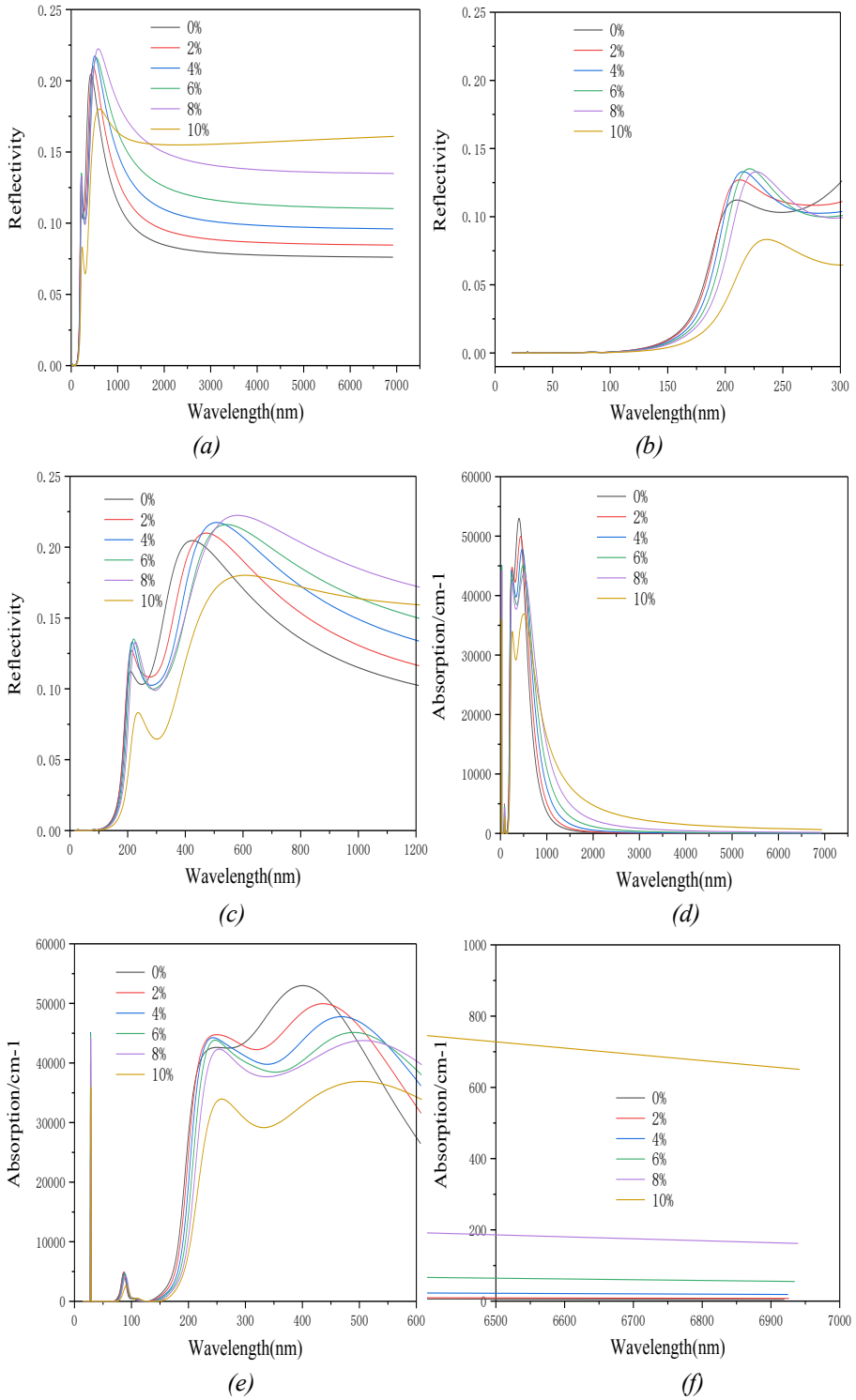


Fig. 7. (a) and (d) are the reflectance and light absorption coefficient of the ReS2-adsorbed S atom system under the tensile deformation of 0% to 10%, (b) and (c) are the local enlarged views of (a), (e)) and (f) are partial enlarged images of (d).

4. Conclusion

This paper investigates the structural stability, electronic structure and optical properties of monolayer ReS2-adsorbed S-atom systems under different amounts of tensile deformation based on density functional theory, including the adsorption energy, band structure, density of states, light reflectivity, optical properties and absorption coefficient of the system. From the calculation results of adsorption energy, it can be seen that the tensile deformation will continuously improve the stability of the structure, in contrast, tensile deformation has little impact on the structural stability of the ReS2-adsorbed S-atom system.

The analysis of the electronic structure shows that with the enhancement of the tensile deformation, the band gap values of the intrinsic ReS2 system and the S atom-adsorbed ReS2 system have a relatively large decrease, in which the intrinsic ReS2 system is more sensitive to tensile deformation, and shows metalloid properties when the tensile deformation is 10%; the tensile deformation increases the summit density of states at different positions of the adsorption system, and the s-state electrons, p-state electrons and d-state electrons of the adsorption system all contribute to the total density of states. In the study of optical properties, it was found that the growth rate of light absorption coefficient and light reflectivity reduced with the enhancement of tensile deformation, and affected by the increase of tensile deformation, both the light absorption summit and light reflection summit appeared red shift.

Acknowledgements

This work is supported by the Planning project of Liaoning Provincial Department of Education (Grant No. LZGD2019003).

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