Adsorption of SF₆ Decomposition Products by the S Vacancy Structure and Edge Structure of SnS₂: A Density Functional Theory Study

Jincong Wang, Xiaoxing Zhang,* Li Liu, and Zengting Wang

ABSTRACT: Detecting the composition and concentration of SF₆ decomposition products is an effective method to evaluate the state of gas-insulated switchgear. Based on density functional theory, in this work we investigated the adsorption properties of four typical SF₆ decomposition products (H₂S, SO₂, SOF₂, SO₂F₂) on an SnS₂ S vacancy structure (SnS₂-Sv) and SnS₂ edge structure (SnS₂-edge). By calculating the adsorption energy, charge transfer, and comparing the density of states (DOS) of each system before and after the adsorption of gas molecules, the physical and chemical interactions between SnS₂ with different structures and gas molecules were investigated. The results show that SnS₂-Sv has the largest adsorption energy for SO₂ and has obvious chemical interactions. The S vacancy can effectively capture an O atom in SO₂, causing SO₂ to firmly adsorb in the S vacancy. In addition, the adsorption of the four gases on the SnS₂-edge is physical adsorption, in which the 50% S edge structure has the largest adsorption energy for H₂S, reaching −0.52 eV, and there is also a large charge transfer between the 50% S edge structure and H₂S. Although the adsorption energy of SnS₂-edge to the four gases is smaller than SnS₂-Sv, it is still greater than the pristine SnS₂. This paper explores the adsorption properties of SnS₂-Sv and SnS₂-edge for SF₆ decomposition products, providing insights for the development of SnS₂-based gas sensors.

1. INTRODUCTION

In the power industry, sulfur hexafluoride (SF₆) gas is a kind of insulating medium with good insulation performance and arc extinguishing performance, which has been widely used in gas insulating equipment. However, in practical engineering applications, there are inevitably some insulation defects in electrical equipment, such as metal burr, suspended conductive particles, etc. These defects will cause partial discharge1,2 or partial overheating inside the equipment, which will lead to the decomposition of SF₆ gas and generate a series of low-fluoride sulfides (SFₓ, x = 1−5). These low-fluoride sulfides easily react with microwater and micro-oxygen to produce HF, H₂S, SO₂, SOF₂, SO₂F₂, and other gases.3−6 These gases have a strong corrosive effect on the insulating materials or metal materials inside the equipment, which will accelerate the deterioration of insulation and eventually lead to the sudden breakdown of the equipment. Thus, the monitoring of SF₆ typical decomposition products can effectively carry out incipient fault diagnosis and ensure the stable operation of electrical equipment.

The carrier migration and heat diffusion of two-dimensional materials, such as graphene,12−14 transition metal dichalcogenides (TMDCs),15,16 MXenes,17,18 hexagonal boron nitride,19,20 etc., are confined to the two-dimensional plane,7−11 which makes these materials exhibit many strange properties. Among them, TMDCs are MX₂-type two-dimensional materials, where M is the transition metal (Mo, W, etc.) and X is the chalcogen (S, Se, Te). TMDCs are generally layered materials, and each layer of the repeating unit contains a layer of transition metal, which is added between two layers of S (Se, Te) atoms. The band gap of many TMDCs is in the range of 1−2 eV and increases as the number of layers
decreases. When the number of layers is reduced to a monolayer, the band structure also changes from the indirect band gap to the direct band gap. The unique band structure makes them very promising electronic and optical materials used in many precision devices. In addition, in the field of gas sensing, TMDCs have also received extensive attention due to their outstanding performance. The few-layer MoS2 nanosheets (FLMNs) prepared by mechanical exfoliation have excellent response and recovery performance to NO2 gas at room temperature. Some scholars have also successfully prepared a low-cost and efficient NH3 gas sensor by using inkjet printing with high-concentration aqueous dispersion of MoS2. The WS2 nanosheet-based sensor shows an excellent response and good selectivity to NH3 at room temperature, and the response will increase with the increase of humidity in the air. In theoretical calculation, some scholars found that MoTe2 had selectivity and sensitivity to SO2 in SF6 decomposition products based on first-principles calculation. In addition, other MX2-types of TMDCs also have excellent performance, such as SnS2. SnS2 shows an excellent two-dimensional structure, with a band gap of 1.8 eV, an outstanding carrier mobility of 50 cm2 V−1 s−1, and a high on/off ratio, which has great application prospects in field-effect transistors. In the field of gas sensing, some scholars use the liquid exfoliation method to detect low concentrations of the NO gas. Other scholars prepared SnS2 by the high-energy ball-milling (HEBM) method with extremely high response to NO2 gas and reasonable response/recovery time. The above research results indicate that SnS2 has potential as a gas-sensing material.

Under normal circumstances, in the exfoliation process of a monolayer, it will inevitably cause atomic detachment and form some vacancies, and these vacancies will significantly change the electronic properties of the material surface, enhance the chemical reaction, and improve its adsorption performance to gas molecules. Therefore, based on density functional theory, this work establishes the most stable adsorption model of H2S, SO2, SOF2, and SO2F2 on SnS2-Sv and SnS2-edge. We comprehensively investigated the interaction behavior between different SnS2 structures and SF6 decomposition products by calculating the adsorption energy, charge transfer, density of states, charge density difference, and recovery time. This work provides a theoretical basis for the application of gas sensors based on different SnS2 structures in the detection of SF6 decomposition products.

## 2. RESULTS AND DISCUSSION

### 2.1. Adsorption Analysis of SF6 Decomposition Products on SnS2-Sv

For TMDCs, the vacancy is usually an active site. In other words, the active site of SnS2-Sv is the S vacancy, as shown in Figure 1. Therefore, in this paper, the adsorption sites of four SF6 decomposition products on SnS2-Sv were set above the S vacancy, and the four molecules were made to approach the S vacancy from different angles. By comparing the adsorption energy, the most stable adsorption structures of the four gases on SnS2-Sv were obtained. For the H2S gas, three different initial adsorption structures can be set up. H2S placed horizontally above the S vacancy or H2S placed vertically with one of the H or S atoms placed above the S vacancy. The molecular structure of SO2 is similar to that of H2S, both of which are V-shaped, and thus, the initial adsorption structure can be set up the same as that of H2S. SOF2 gas has two initial adsorption structures, which are S atoms up/down close to S vacancies. The initial adsorption direction of SO2F2 gas includes two kinds, one is the F atom near the S vacancy and the other is the O atom near the S vacancy.

The most stable adsorption structures of the four SF6 decomposition products on SnS2-Sv are shown in Figure 2, and the adsorption energy, charge transfer, and adsorption distance are shown in Table 1. H2S tends to be horizontally adsorbed to the vacancy of SnS2-Sv where the closest distances between H and S atoms in H2S and Sn atoms in SnS2-Sv were 3.514 and 3.511 Å, respectively. It is worth noting that the six-
between H$_2$S and SnS$_2$-S$_v$. Interestingly, when SnS$_2$-S$_v$ adsorbs H$_2$S, the DOS shows four adsorption systems, DOS, and PDOS (the lower part is DOS and the upper part is PDOS). In the H$_2$S adsorption system, when SnS$_2$-S$_v$ adsorbs H$_2$S, the DOS will move to the right, the peak at 1 eV disappears, and a new peak appears at $-$14 eV. According to PDOS, the new peak is mainly related to the H 1s orbital. Moreover, from $-$6 to $-$2 eV, the S 3p orbital and the Sn 5p orbital have different degrees of overlap, and near 3 eV, the H 1s orbital, S 3p orbital, and Sn 5p orbital were almost completely overlapped, which indicates the existence of orbital hybridization, implying a strong interaction between SnS$_2$-S$_v$ and H$_2$S. In the SO$_2$ adsorption system, when SnS$_2$-S$_v$ adsorbs SO$_2$, new peaks appear at $-$12 and $-$6 eV. From $-$8 to $-$2 eV, near the Fermi level (0 eV), the O 2p orbital, Sn 5s orbital, and Sn 5p orbital have a large area of overlap peaks, indicating that there is strong hybridization between O atoms and Sn atoms, which also supports the formation of new O$-$Sn bonds. Since in the adsorption mechanism of SOF$_2$ and SO$_2$F$_2$, the O atom is close to the S vacancy, the hybridization between the orbitals is similar to the SO$_2$ adsorption system. From $-$7 to $-$4 eV, the Sn 5s orbital and Sn 5p orbital overlap with the O 2p orbital; however, the area of the overlapping peaks is smaller than that of the SO$_2$ adsorption system, therefore, the possibility of forming new chemical bonds is low.

### 2.2. Adsorption Analysis of SF$_6$ Decomposition Products on the SnS$_2$-edge

The structure of SnS$_2$ is the IT type. According to recent reports on the edge structure of IT TMDCs,$^{46}$ three different edge structures have been established in this paper, as shown in Figure 5 the edge structure with 0% S covering atoms (0% S, 100% Sn); the edge structure with 50% S atom coverage (50% S, 50% Sn); the edge with a 100% S coverage structure (100% S, 0% Sn), respectively. After geometrically optimizing the three edge structures, considering the difference in the molecular structure between the S atom and the O atom, resulting in the extension of the S$-$O bond length. However, far away from the S vacancy, there is no obvious electron depletion between the O atom and the S atom, so the bond length of the S$-$O bond far away from the S vacancy does not change significantly. For the two gases SOF$_2$ and SO$_2$F$_2$, the charge transfer mechanism is similar to the H$_2$S adsorption system, both of which were obvious electron depletion above the Sn-n bond in the S vacancy; thus, the Sn$-$S bond was also extended. In summary, the electron in the four adsorption systems has been redistributed.

By calculating and comparing the changes of DOS before and after SnS$_2$-S$_v$ adsorption of the four gases, the interaction between the four gases and SnS$_2$-S$_v$ can be further explored. Figure 4a$-$d shows four adsorption systems, DOS, and PDOS.

| Table 1. SnS$_2$-S$_v$ Adsorption Parameters |
|---------------------------------------------|
| adsorption structure | adsorption energy (eV) | charge transfer (e) | adsorption distance (Å) |
| SnS$_2$-S$_v$/H$_2$S | $-$0.69 | 0.0379 | 3.511 (H$_2$S$-$Sn) |
| SnS$_2$-S$_v$/SO$_2$ | $-$1.11 | $-$0.1963 | 3.545 (S$_v$O$_2$$-$Sn) |
| SnS$_2$-S$_v$/SOF$_2$ | $-$0.63 | 0.0179 | 4.248 (S$_v$OF$_2$$-$Sn) |
| SnS$_2$-S$_v$/SO$_2$F$_2$ | $-$0.58 | 0.0277 | 4.198 (S$_v$SO$_2$F$_2$$-$Sn) |

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of each gas and the difference in the three edge structures, multiple adsorption systems were established.

Table 2 shows the adsorption energy, charge transfer, and adsorption distance of different adsorption systems. By comparing the adsorption energy in Table 2, it can be seen that among the three edge structures, the 50% S edge structure has better adsorption performance for the four gases, and the 100% S edge structure has weaker adsorption performance for the four gases than the other two edge structures. For the four gases, the adsorption performance of the three edge structures for H₂S is better than for the other three gases, and the adsorption energy of the 50% S edge structure for the H₂S gas is the largest, reaching −0.52 eV. In contrast, the three edge structures have weaker interactions with the two gases SO₂F₂ and SO₂F₂, and the adsorption energy is not higher than −0.3 eV. When the four gas molecules are adsorbed on different edge structures, the charge transfer will be different. On the 0% S edge structure, SO₂ gains electrons and the other three gases lose electrons. On the 50% S edge structure, all four gases lose electrons. On the 100% S edge structure, H₂S gains electrons, and SO₂F₂, SO₂F₂, and SO₂F₂ lose electrons.

Figure 4. DOS and PDOS of the four adsorption systems: (a) H₂S adsorption system, (b) SO₂ adsorption system, (c) SOF₂ adsorption system, and (d) SO₂F₂ adsorption system.

Figure 5. SnS₂-edge structures: (a) 0% S structure, (b) 50% S structure, and (c) 100% S structure.
and the other three gases lose electrons. Figure 6 shows the most stable adsorption structure and CDD of each adsorption system. According to the adsorption distance, it can be seen that the adsorption mechanisms of the three gases SO2, SOF2, and SO2F2 tend to be in O atoms close to the 0% S edge structure and 50% S edge structure. According to CDD, it can be seen that except for the two adsorption systems of 100% S/SOF2 and 100% S/SO2F2, all other adsorption systems have undergone electron redistribution.

We selected three structures with the largest adsorption energy for DOS analysis, namely, H2S adsorbed on the 0% S edge structure, 50% S edge structure, and 100% S edge structure, as shown in Figure 7. After the three edge structures adsorbed H2S, the DOS did not change significantly and there were only peak height differences in some positions. For the 0% S edge structure, the Sn 5s orbital and the S 3p orbital overlap significantly from −6 to −5 eV, and the Sn 5p orbital and the S 3p orbital have peak overlaps from −3 to 0 eV. For the 50% S edge structure, the Sn 5s orbital and S 3p orbital also have a large degree of peak overlap between −6 and −5 eV, while the Sn 5p orbital and S 3p orbital have a peak overlap between −5 and 0 eV. The degree of overlap is slightly greater than the 0% S edge structure, which also proves that the adsorption energy of H2S on the 50% S edge structure is greater than the 0% S edge structure. For the 100% S edge structure, the H 1s orbital, the S 3p orbital, and the Sn 5p orbital overlap between −5 and −3 eV, and the S 3p orbital and the Sn 5p orbital overlap slightly from −2.5 to 0 eV. In general, the three edge structures mainly interact with the S atoms in H2S.

Table 2. SnS2-Sv Adsorption Parameters

| adsorption structure | adsorption energy (eV) | charge transfer (e) | adsorption distance (Å) |
|----------------------|------------------------|---------------------|-------------------------|
| 0% S/H2S             | −0.36                  | 0.0399              | 2.745 (H−Sn in SnS2)    |
| 0% S/SO2             | −0.34                  | −0.0185             | 3.193 (O−Sn)            |
| 0% S/SOF2            | −0.28                  | 0.0029              | 3.490 (O−Sn)            |
| 0% S/SO2F2           | −0.23                  | 0.0128              | 3.264 (O−Sn)            |
| 50% S/H2S            | −0.52                  | 0.1761              | 2.933 (S in H2S−Sn)     |
| 50% S/SO2            | −0.37                  | 0.0744              | 2.923 (O−Sn)            |
| 50% S/SOF2           | −0.29                  | 0.0221              | 2.945 (O−Sn)            |
| 50% S/SO2F2          | −0.23                  | 0.0440              | 3.127 (O−Sn)            |
| 100% S/H2S           | −0.28                  | 0.0652              | 2.687 (H−S in SnS2−edge) |
| 100% S/SO2           | −0.27                  | −0.0899             | 3.065 (S−S in SnS2−edge) |
| 100% S/SOF2          | −0.17                  | −0.0227             | 3.270 (F−S in SnS2−edge) |
| 100% S/SO2F2         | −0.18                  | −0.0009             | 3.414 (F−S in SnS2−edge) |

Figure 6. Adsorption structure and CDD (the isosurface is 0.005 e/Å3) of the four gases on the SnS2 edge (a1−a4) 0% S structure, (b1−b4) 50% S structure, and (c1−c4) 100% S structure.

2.3. Comparison of the Adsorption Performance of SF6 Decomposition Products on Different Structures of SnS2. We calculated the adsorption energies of the four gases on pristine SnS2 to evaluate whether SnS2-Sv and SnS2-edge have improved adsorption properties for SF6 decomposition products. The adsorption energies of H2S, SO2, SOF2, and SO2F2 on pristine SnS2 are −0.17, −0.18, −0.16, and −0.15 eV, respectively, which are consistent with the studies of other scholars37 and also prove that our calculations are correct. Figure 8 shows the comparison of the adsorption energies of the four gases on pristine SnS2, SnS2-Sv, and SnS2-edge. It can be clearly seen that SnS2-Sv can effectively improve the adsorption performance of the four gases, especially the adsorption of SO2. SnS2-edge can also improve the adsorption performance of the four gases to different degrees. The 0% S edge structure and 50% S edge structure can effectively improve the adsorption performance of H2S and SO2, among which the 50% S edge structure has the best adsorption performance for H2S. However, the adsorption performance of the four gases with the 100% S edge structure was not

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significantly improved, especially for SOF$_2$ and SO$_2$F$_2$. In general, SnS$_2$-S$_v$ and SnS$_2$-edge are beneficial to improve the adsorption performance of SF$_6$ decomposition products.

2.4. Evaluation of the Values of SnS$_2$-S$_v$ and SnS$_2$-Edge as the Gas-Sensing Material to SF$_6$ Decomposed Products. The value of SnS$_2$-S$_v$ and SnS$_2$-edge as gas-sensitive materials can be evaluated by the recovery time. The recovery time refers to the process of gas desorption from the sensor surface, which can be calculated by the van’t Hoff Arrhenius equation.\(^\text{38}\)

$$\tau = A^{-1} \exp\left(\frac{E_b}{k_B T}\right)$$

where \(\tau\) is the recovery time; \(A\) is the attempt frequency factor, which is about \(10^{12} \text{ s}^{-1}\);\(^{39,40}\) \(E_b\) is the potential barrier that needs to be overcome for desorption, which is equal to the negative of the adsorption energy; \(k_B\) is the Boltzmann constant; and \(T\) is the thermodynamic temperature. For the SnS$_2$-edge, the 50% S/H$_2$S adsorption system has the longest recovery time, which is about 619 \(\mu\)s. The adsorption energy of other adsorption systems does not exceed \(-0.37\) eV, so the desorption time will be shorter. For SnS$_2$-S$_v$, when the SO$_2$ adsorption system works at 298 K, the recovery time is \(5.84 \times 10^5\) s, and when the temperature increases to 398 K, the recovery time is shortened to 112.54 s. In other words, when the temperature is in the range of 298–398 K, the recovery time of the SO$_2$ adsorption system can be adjusted between different orders of magnitude, which means that SnS$_2$-S$_v$ is a promising gas-sensitive material for detecting SO$_2$.

3. CONCLUSIONS
In this work, we considered the adsorption performance of SF$_6$ decomposition products on SnS$_2$-S$_v$ and SnS$_2$-edge. Based on
density functional theory, we calculated the adsorption energy, charge transfer, and differential charge density, and compared the DOS before and after the adsorption of gas molecules in each system and comprehensively investigated the physical and chemical interactions between gas molecules and SnS2 with different structures. In addition, we also calculated the adsorption performance of the four gases on pristine SnS2 and compared the adsorption energy to evaluate whether the adsorption performance of SF6 decomposition products on SnS2-Sv and SnS2-edge can be improved. The results showed that the S vacancy of SnS2-Sv can effectively capture the O atoms in SO2, SOF2, and SO2F2, and SO2 will directly enter the S vacancy, causing the adsorption energy of the SO2 adsorption system reach −1.11 eV, which is greater than those of the other three gases. In addition, SnS2-Sv also has a suitable recovery time for SO2; when the temperature is 398 K, the recovery time is 112.54 s. SnS2-edge has three edge structures, which are the 0% S edge structure, 50% S edge structure, and 100% S edge structure. The three edge structures all have good adsorption properties for H2S, and there is a large charge transfer between the 50% S edge structure and H2S. However, the 100% S edge structure has weak adsorption of SOF2 and SO2F2. By comparing the adsorption energies of the four gases on SnS2-Sv, SnS2-edge and pristine SnS2, it can be found that SnS2-Sv and SnS2-edge are beneficial to improve the adsorption performance of the four gases. Our research provides insights for the further development of SnS2-based gas sensors.

4. COMPUTATIONAL METHODS

All geometric optimization and electronic calculations were based on the DMOl3 package. The generalized gradient approximation (GGA) method and Perdew–Burke–Ernzerhof (PBE) functional were used to determine the electron exchange correlation function. The double numerical polarization (DNP) was selected as the atomic orbital basis set and the DFT semiconductor pseudopotential (DSSP) was used to determine the relativistic effect of heavy elements. The DFT-D2 method was used to determine the van der Waals force and long-range interactions. The cutoff radius was set to 5.0 Å. For the geometric optimization of all structures, the convergence standard was set as follows: the energy difference between the two geometric optimization values was less than 1.0 × 10−5 Ha, the force of each atom was less than 0.002 Ha/Å, and the maximum displacement distance of each atom was less than 0.005 Å.

The lattice parameter of bulk SnS2 was calculated to be 3.69 Å. This is consistent with the research of other scholars. By cleaving the 0 0 1 surface of bulk SnS2, a 3 × 3 × 1 single layer SnS2 was established, and the vacuum layer was set at 15 Å on the z-axis to avoid the interaction between adjacent layers. To simulate SnS2 with the S vacancy, the perfect SnS2 was geometrically optimized and then an S atom was removed (including 17 S atoms and 9 Sn atoms) and geometrically optimized again. For all geometrical optimizations, the Monkhorst Pack grid k-point in the Brillouin zone was set as 4 × 4 × 1, and a more accurate k-point of 8 × 8 × 1 was set for electronic calculations.

SnS2 is a CdI2 structure (1T structure) with the corresponding space group P6/m1, and the Sn atom is octahedrally coordinated by the S atoms. The edge structure only exists on the (1 0 0) crystal plane, and there are three different structures on the edge: 0% S atoms on the edge (0% S, 100% Sn), 50% S atoms on the edge (50% S, 50% Sn), and 100% S atoms on the edge (100% S, 0% Sn). For the three edge structures, the repeat unit was set as the y-axis and there were four unit cells. The vacuum layer was set as 30 and 15 Å on the x-axis, and z-axis, respectively. The Monkhorst Pack grid k-point in the Brillouin zone was set as 1 × 3 × 1, and a more accurate k-point of 1 × 5 × 1 was set for electronic calculations.

Adsorption energy was used to characterize the adsorption properties of the four gas molecules on SnS2-Sv or SnS2-edge. The calculation formula of the adsorption energy ($E_{ads}$) can be defined as

$$E_{ads} = E_{SnS2-Sv/gas} - E_{SnS2-Sv} - E_{gas}$$

(2)

$$E_{ads} = E_{SnS2-edge/gas} - E_{SnS2-edge} - E_{gas}$$

(3)

where $E_{SnS2-Sv/gas}$ and $E_{SnS2-edge/gas}$ represent the total energy of the SnS2-Sv adsorbed gas molecules and the total energy of the SnS2-edge-adsorbed gas molecules. $E_{SnS2-Sv}$ and $E_{SnS2-edge}$ represent the total energy of SnS2-Sv and SnS2-edge. $E_{gas}$ represents the total energy of gas molecules.

The charge transfer in each adsorption system was analyzed by the Hirshfeld method, which is determined by the electron density.

$$Q = -\int \left( \sum \rho_0(r) - \sum \rho_0^T(r) \right) \delta(r) dr$$

(4)

Here, $\rho_0(r)$ represents the electron density in each atom’s isolated state, $\sum \rho_0^T(r)$ is the sum of $\rho_0(r)$, and $\delta(r)$ represents the electron density of the entire system. The charge transfer ($Q_T$) can be defined as

$$Q_T = Q_{after} - Q_{before}$$

(5)

where $Q_{after}$ represents the electrons of gas molecules after adsorption and $Q_{before}$ represents the electrons of gas molecules before adsorption. If the value of $Q_T$ is positive, it indicates that during the adsorption process, the gas molecules lose electrons and the crystal gains electrons, and vice versa.

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Notes
The authors declare no competing financial interest.

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