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NO₂ Adsorption Sensitivity Adjustment of As/Sb Lateral Heterojunctions through Strain: First Principles Calculations

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Abstract: Strain engineering is an effective way to adjust the sensing properties of two-dimensional materials. In this paper, lateral heterojunctions (LHSs) based on arsenic and antimony have been designed along the armchair (AC) or zigzag (ZZ) edges. The adsorption and sensing characteristics of As/Sb LHSs to NO₂ before and after applying different types of strain are calculated by first principles. The band gaps of all As/Sb heterostructures are contributed by As-p and Sb-p orbitals. In addition, the adsorption energy of As/Sb ZZ-LHS with −4% compression strain is the largest. Furthermore, its work function changes significantly before and after the adsorption of NO₂. Meanwhile, strong orbital hybridizations near the Fermi level are observed and a new state is yielded after applying compressive strain. These results indicate that the As/Sb LHS with ZZ interface under −4% compression strain possesses the best sensing properties to NO₂. This work lays the foundation for the fabrication of high-performance NO₂ gas sensors. High-performance gas sensors can be used to track and regulate NO₂ exposure and emission, as well as to track NO₂ concentrations in the atmosphere and support the assessment of air quality.

Keywords: lateral heterostructure; first principles calculations; strain; adsorption; NO₂ gas sensing



Citation: Yang, L.; Wang, D.; Fang, D.; Yan, H.; Zhai, Y.; Chu, X.; Li, J.; Fang, X. NO₂ Adsorption Sensitivity Adjustment of As/Sb Lateral Heterojunctions through Strain: First Principles Calculations. *Crystals* **2023**, *13*, 1325. <https://doi.org/10.3390/cryst13091325>

Academic Editor:
Sławomir Grabowski

Received: 29 July 2023

Revised: 18 August 2023

Accepted: 23 August 2023

Published: 30 August 2023



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1. Introduction

In recent years, the harmful gases produced in automobile exhausts and industrial production have caused significant risks to the safety of people's life and property. NO₂ pollution in the atmosphere can seriously endanger human health, weaken lung function and reduce the ability of the respiratory system to resist diseases. In addition, a large number of NO₂ emissions will cause severe destruction in the ecological environment, such as the formation of acid rain and photochemical smog [1–4]. Therefore, the monitoring of NO₂ is indispensable. The sensor's sensing mechanism detects the charge transfer between the sensor and the gas molecule or resistance difference in the sensor before and after gas absorption under certain conditions. The sensitive materials useful for NO₂ sensors mainly contain nanomaterials, such as nanoparticles, nanowires and two-dimensional materials. For example, Ren et al. constructed a ZnO–SnO₂ heterojunction to monitor the NO₂ centration, and the sensitivity of ZnO–SnO₂ heterojunctions is relatively highest at 180 °C [5]. In addition, Choi synthesized porous zinc oxide nanosheets using traditional solvothermal methods and verified their excellent response properties for NO₂ at 200 °C [6]. In recent years, researchers have developed new materials for high-performance gas sensor applications.

In the field of gas sensing, two-dimensional materials have great potential to be the new generation of sensing materials because of their high surface volume ratio and unique physical and chemical properties [7,8], such as graphene [9–11], transition metal dichalcogenides compounds (TMDs) [12–14], and transition metal carbides (MXenes) [15–18]. In order to improve the sensitivity of gas sensors, two-dimensional heterostructure material

systems are constructed [19,20]. Heterostructures mainly include vertical heterostructures (VHSs) and lateral heterostructures (LHSs). The van der Waals force between layers, unaffected by lattice mismatch, allows VHSs to be built vertically through stacking layers of various two-dimensional materials. The performance of vertical heterostructures is severely constrained due to non-radiative recombination centers caused by high-density defects introduced during the manufacturing process. Meanwhile, it is also limited by weak electron transmission between stacking layers [21–23]. The lateral heterostructures (LHSs) [24–26] are connected by covalent bonds, ensuring electron transmission performance. The LHSs have been designed or fabricated for photodetection and gas-sensing because of their advantages of more vital chemical interaction and exposed active interfaces. The characteristics of fewer interface defects and low lattice mismatch can effectively improve the charge transfer ability perpendicular to the interface, which enables the LHSs to achieve high gas sensitivity. However, the studies on lateral heterostructures are still at the initial stage and the sensors based on LHSs cannot be applied in practice. Therefore, it is of great significance to enhance their sensing performances.

Strain engineering has already been confirmed to be an effective way to improve the properties of photonic and electronic devices [13,27–29]. In our previous work, the band gaps and band types of As/Sb LHSs have been adjusted by applying tensile or compressive strains [23,30,31]. Meanwhile, the adjustment of gas sensing properties is achieved by modifying the surface structure of the substrate material to change the adsorption between the substrate material and the gas. The strain-introduced adjustment of gas sensing characteristics has been realized in various two-dimensional materials, such as MoSSe [14] and InP₃. In the adsorption system of formaldehyde and InP₃, the absolute value of adsorption energy has been dramatically increased after applying 4% strain on a single-layer InP₃ [32]. Hence, it is essential to enhance the sensing performances of LHSs by applying strains [33–35].

In this paper, As/Sb lateral heterojunctions with four atomic chains along the armchair (AC) and zigzag (ZZ) interfaces were constructed. Their adsorption properties were calculated by using the first principles calculations. The adsorbed gas configuration and band structure changes were investigated when various strains were applied to the interfaces. It is worth noting that the adsorption energy of all As/Sb LHSs significantly increases after applying compressive strain, indicating that the As/Sb LHSs under compressive strain are more suitable for acting as gas-sensing materials. In addition, the total density of states (TDOS), the partial density of states (PDOS), and the charge transfer (ΔQ) were analyzed in detail. The degrees of orbital hybridization were greatly enhanced, and charge transfers were significantly increased upon applying compressive strain. Hence, the variation in the density of states near the Fermi level is considered the main reason for gas-sensing performance enhancement. Furthermore, it is found that the As/Sb ZZ-LHS possesses the highest sensitivity to NO₂ under compressive strain. This is significant for fabricating high-performance NO₂ gas sensors with excellent adsorption properties under strain.

2. Computational Details

The Vienna ab initio simulation package (VASP) based on density functional theory (DFT) is used to calculate the sensing performance of As/Sb LHSs [36,37]. The projection-augmented wave potentials (PAW) method is used to describe the interaction between electrons and ions, and the generalized gradient approximation (GGA) of Perdew–Burke–Ernzerhof (PBE) is used to describe the electron exchange–correlation energy [38]. The semiempirical dispersion-corrected DMol³ scheme, proposed by Grimme, to treat long-range van der Waals interactions among atomic layers was adopted [39–41]. To avoid layer-to-layer interactions, the vacuum layer was set to 15 Å. The As 2s²2p⁴ and Sb orbitals were set as valence states, and the cut-off energy of the plane wave basis was set at 600 eV. The convergence criteria for energy (converged to 1.0×10^{-5} eV per atom) and force (converged to 0.01 eV Å^{−1}) were set for geometry optimization. Brillouin zones (BZs) are sampled by a grid of k-points with a constant spacing of $2\pi \times 0.04$ Å^{−1}. Lastly, the

electronic band structure, density of states (DOS), valence band maximum (VBM), and partial charge of conduction band minimum (CBM) for each 2D As/Sb LHS in the model were detailed and analyzed before and after calculation.

3. Results and Discussion

Similar to curved silicene and germanene, arsenene and antimonene possess curved honeycomb structures [42]. Both of them are hexagonal lattices and contain two kinds of atomic configuration boundaries: armchair and zigzag. Therefore, two kinds of atomic arrangement exist on the constructed As/Sb LHS interface, labeled as AC-LHS and ZZ-LHS, respectively. As shown in Figure S1, the As and Sb atomic chains are perpendicular to the boundary and alternately stacked to form a periodic heterostructure. According to the electron orbital theory, the interaction between As and Sb atoms is mainly limited around the interface. The number of atomic chains selected in this work is 4. The top and side views of the optimized structure of NO₂ adsorption on the As/Sb LHSs are shown in Figure 1. After the optimization calculation, we found that the most stable adsorption sites of NO₂ molecules on these six LHSs were located above the interface. The interface region is highlighted in yellow; Figure 1a,d represent the structures under −4% compressive strain, while Figure 1c,f show those under 4% tensile strain. It can be seen that the As/Sb AC-LHSs have no deformation when tensile strains are applied, slight deformation when no strain is applied, and relatively obvious deformation under compression strain. Hence, the absorption system can bear tensile strain rather than compressive strain. Similarly, the structural changes of As/Sb ZZ-LHSs have the same rule as those of As/Sb AC-LHSs. However, no deformation occurs for the LHSs without NO₂ adsorption, whether the strains are applied or not, as shown in Figure S1. These results indicate that the deformation here may be attributed to the degeneration of the covalent bond caused by the charge transmission between the gas molecule and the base material.

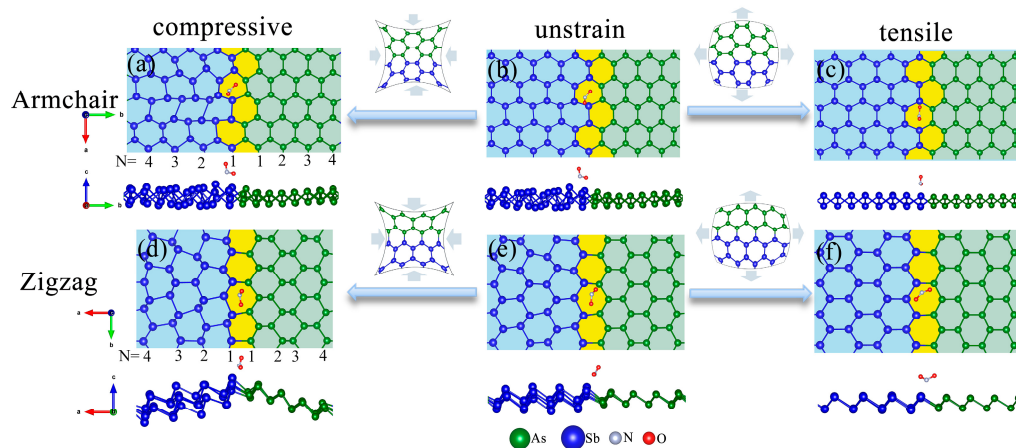


Figure 1. Top and side views of the As/Sb AC-LHS adsorbed NO₂ under (a) compressive strain, (b) unstrained, and (c) tensile strain, and those of the As/Sb ZZ-LHS adsorbed NO₂ under (d) compressive strain, (e) unstrained, and (f) tensile strain.

The formation energy (E_f) can be used as an evaluation index to determine the structural stability and energy stability of the constructed LHSs without NO₂ adsorption. The calculation method for E_f is defined as follows:

$$E_f = \frac{E_{AB} - E_A - E_B}{N} \quad (1)$$

where E_{AB} represents the energy of As/Sb LHSs, E_A and E_B represent the total energy of As and Sb atoms, respectively, and N represents the number of atoms. As shown in Table 1, the formation energies of As/Sb AC-LHSs and As/Sb ZZ-LHSs under three different strains of

−4%, 0% and 4% were calculated, respectively. It can be seen that the formation energy of the two interfaces of As/Sb LHSs under different strain conditions was negative, which indicates that the predicted As/Sb LHSs were favorable and stable even under strain. As shown in Table 1, although the formation energy decreased slightly after applying compressive and tensile strains, the structures of As/Sb AC-LHSs and As/Sb ZZ-LHSs were also stable.

Table 1. Formation energy of As/Sb AC-/ZZ-LHSs under different strains.

Interface	Formation Energy (eV)		
	−4%	4%	4%
As ₄ /Sb ₄ AC-LHS	−2.73	−2.76	−2.74
As ₄ /Sb ₄ ZZ-LHS	−2.70	−2.73	−2.71

Generally speaking, the stability of the adsorbed gas molecules can be characterized by the adsorption energy, adsorption distance and charge transfer. Therefore, the adsorption energy was calculated to predict the adsorption intensity of NO₂ molecules on the As/Sb LHSs surface. The adsorption energy is defined as follows:

$$E_a = E_{total} - (E_{sub} + E_{gas}) \quad (2)$$

where E_{total} is the total energy of the NO₂-As/Sb LHS adsorption system, E_{sub} is the energy of the monolayer As/Sb LHSs, and E_{gas} is the energy of isolated gas molecules. According to the definition, a negative value of E_a indicates that the adsorption process is an exothermic reaction and can proceed spontaneously. Furthermore, the more negative the value of E_a is, the greater the adsorption intensity is [43,44].

In order to compare the adsorption intensities of all LHSs, the differences in adsorption energy and the variation in work function are plotted in Figure 2. As shown in Figure 2a, the adsorption energies in all cases are negative, indicating that the adsorption of NO₂ on As/Sb LHSs is an exothermic process with thermodynamic stability, which is beneficial to the gas sensor. As/Sb LHSs under −4% compressive strain, regardless of interface configurations, possess larger adsorption energies than those under other conditions. The adsorption energy of the As/Sb AC-LHS under compressive strain is −1.64 eV, followed by the unstrained system at −0.51 eV, and the adsorption energy of −0.28 eV is achieved under tensile strain. Similarly, the adsorption energy of the As/Sb ZZ-LHS under compressive strain is −2.79 eV, followed by the unstrained system at −0.67 eV. The adsorption energy under tensile strain is −0.19 eV, the lowest absolute value among the six conditions. It is evident that As/Sb ZZ-LHS has the largest adsorption energy value among all configurations for adsorbing NO₂. Hence, the adsorption intensity of As/Sb ZZ-LHS in relation to NO₂ molecules under −4% compressive strain is the strongest.

The work functions of the As/Sb LHSs before and after applying strain are shown in Figure 2b. The pink line represents the structures with NO₂ molecule adsorption, while the blue line represents those without NO₂ molecule adsorption. From Figure 2, it can be seen that when As/Sb AC-LHSs and As/Sb ZZ-LHS do not adsorb gas molecules, the work function significantly decreases when compressive strain is applied, and increases significantly when tensile strain is applied. For the As/Sb AC-LHS- and As/Sb ZZ-LHS-adsorbed gas molecules, the change in work function after applying compression and tensile strain is similar to that when not adsorbed. Additionally, it is worth noting that, when −4% compressive strain is applied, it is evident that the work functions of As/Sb AC-LHS and As/Sb ZZ-LHS, which are 0.61 eV and 0.54 eV, respectively, change significantly before and after NO₂ adsorption. Theoretically, the greater the differences in work function before and after adsorption, the higher the systems' sensitivity to NO₂. Combined with the adsorption energy, the As/Sb ZZ-LHS under −4% compressive strain has the highest sensitivity to NO₂ gas molecules, and has the potential to be used as a NO₂ gas sensor according to the interaction force.

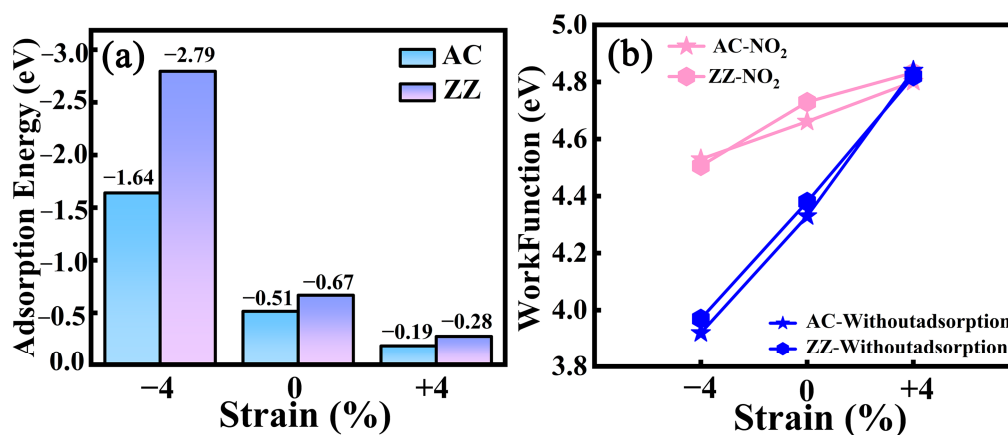


Figure 2. The (a) adsorption energy and (b) work function of As/Sb LHSs at armchair and zigzag interfaces under -4% compressive strain, no strain and 4% tensile strain, respectively.

To further study the gas sensing properties of As/Sb AC-/ZZ-LHSs, the charge transfer (ΔQ) between all LHSs and NO₂ were calculated through Bader analysis and the nearest adsorption distance ($d_{\text{LHSs-NO}_2}$), as shown in Table 2. In the six NO₂-LHS systems, the calculated charge transfers are negative, indicating that electrons are transferred from LHSs to NO₂. So, the As/Sb LHSs act as charge donors, and NO₂ molecules act as acceptors, causing charge accumulation. Thus, the adsorption of NO₂ molecules can be considered to be similar to the acceptor-doping process. Due to the differences in charge transfers, the adsorption distance between LHSs and NO₂ varies with strain conditions. The minimum adsorption distance of NO₂-As/Sb AC-LHS was about $2.47 \text{ \AA}$. However, after applying compressive or tensile strain, it decreased to $2.42 \text{ \AA}$ or increased to $3.08 \text{ \AA}$. Combined with the adsorption energy of the three strain conditions, we can conclude that the adsorption effect of As/Sb AC-LHS on NO₂ under compressive strain is relatively strong, while the adsorption effect under tensile strain is weak. For NO₂-As/Sb ZZ-LHS, the minimum adsorption distance and strength show similar variations, but the adsorption energy after applying compressive strain is the strongest among the six NO₂-LHSs systems, so the adsorption of NO₂ is the strongest in this case.

Table 2. Calculation results of adsorption of gas molecules on As/Sb LHS: charge transfer amount (ΔQ), the distance between the nearest two atoms between gas molecules and the substrate material $d_{\text{LHSs-NO}_2}$, and the bond angle and N–O bond length of NO₂.

Interface	Substrate	ΔQ (e)	$d_{\text{LHSs-NO}_2}$ ($\text{\AA}$)	Degree of O–N–O ($^\circ$)	$d_{\text{N-O}}$ ($\text{\AA}$)
AC	As ₄ /Sb ₄ -neg	−0.64	2.42	121.9	1.25
	As ₄ /Sb ₄	−0.62	2.47	121.9	1.25
	As ₄ /Sb ₄ -pos	−0.65	3.08	112.1	1.30
ZZ	As ₄ /Sb ₄ -neg	−0.61	2.49	121.6	1.25
	As ₄ /Sb ₄	−0.58	2.48	122.5	1.25
	As ₄ /Sb ₄ -pos	−0.46	2.55	125.7	1.24

Geometric optimization on the free NO₂ molecule was also performed, which showed an N–O bond length of $1.21 \text{ \AA}$ and an O–N–O bond angle of 133.39° . However, after the adsorption of NO₂ molecules, the N–O bond lengths were elongated, and the O–N–O bond angle was compressed. In addition, the interaction between the substrate material and the gas molecules leads to charge transfer during adsorption. These transferred charges gather around NO₂. The repulsion between these electrons leads to the N–O bond length being elongated. After the tensile strain is applied to NO₂-As/Sb AC-LHS, the charge transfer is relatively large, so the N–O bond is elongated from $1.21 \text{ \AA}$ to $1.3 \text{ \AA}$, and the O–N–O bond

angle is compressed from 133.39° to 112.1° , which is similar to the adsorption of NO_2 by a doped black phosphorus carbide monolayer [45].

Generally, gas adsorption can be classified into two types: physical adsorption and chemical adsorption. The former originates from weak van der Waals interactions, while the latter is due to the strong chemical bonds between the adsorbent and the adsorbate. The judgment of adsorption type is mainly based on the adsorption energy and distance. The larger the adsorption energy or the smaller the adsorption distance, the more inclined the adsorption will be towards chemical adsorption. The adsorption distances as a function of adsorption energies between the NO_2 molecule and the LHSs are plotted in Figure 3. When the strain is not applied to NO_2 -As/Sb AC-LHS, NO_2 molecules may be chemically adsorbed onto the LHS due to its medium adsorption energy and small adsorption distance of 2.47 Å. After compressive strain is applied, the adsorption energy of the system increases to -1.64 eV, and the adsorption distance decreases to 2.42 Å, indicating that NO_2 was chemically adsorbed onto the LHS. After tensile strain was applied, the adsorption energy decreased, and the adsorption distance increased to 3.08 Å. Hence, the adsorption type of NO_2 on As/Sb AC-LHS transformed into physical adsorption. Similarly, the NO_2 -As/Sb ZZ-LHS system may be chemically absorbed when no strain is applied. The adsorption energy increases significantly after applying the compressive strain, indicating chemical adsorption. When tensile strain is applied, physical adsorption may occur. It is worth noting that the electron transfer between NO_2 and LHSs during chemical adsorption changes the electron distribution in LHSs, resulting in the deformation of the structure, which is also proven in Figure 1.

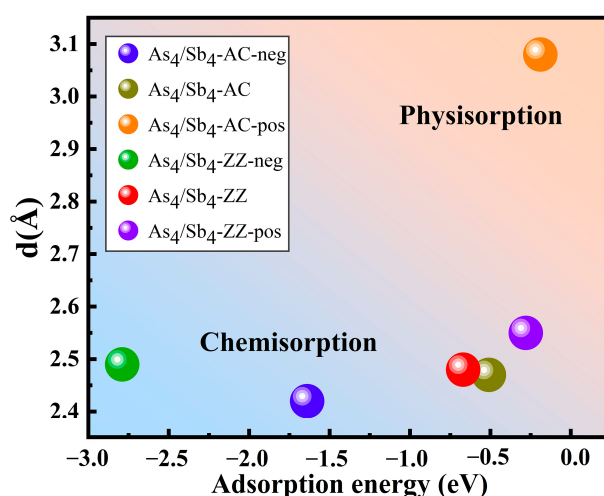


Figure 3. The relationship between adsorption distance and adsorption energy between the NO_2 molecule and substrate LHSs.

In order to further understand the effects of strain on the adsorption properties of As/Sb LHSs for NO_2 molecules, the total electronic density of states (TDOS) and partial density of states (PDOS) of all structures were plotted in Figures 4 and 5. For As/Sb AC-LHS, its conducting band minimum (CBM) moves to the vicinity of the Fermi level after applying a -4% compressive strain, resulting in a smaller band gap. However, after the tensile strain is applied, the VBM of the system remains almost unchanged while the CBM slightly moves towards the high-energy direction, and the band gap becomes wider, as shown in Figure 4c. In contrast, for NO_2 -As/Sb AC-LHS, the valence band maximum (VBM) moves to the Fermi level and crosses the Fermi level after applying compressive strain, resulting in a transition from semiconductor to metallic. Nevertheless, the CBM of the system moves away from the Fermi level, the band gap becomes bigger after applying tensile strain. We compared the TDOS changes of As/Sb AC-LHS before and after absorbing NO_2 under different strains. As shown in Figure 4a, when compressive strain is applied, the electronic state density in the valence band increases after the LHS

absorbs NO_2 , and the VBM moves to the high-energy direction and crosses the Fermi energy level. As shown in Figure 4b, when no strain is applied, the VBM and CBM of the system after absorbing NO_2 move in the Fermi energy level direction, causing the band gap to be significantly compressed. After applying tensile strain, as shown in Figure 4c, and after adsorbing NO_2 , the electronic density of states in the valence and conduction bands remains almost unchanged, but the band gap decreases. For As/Sb ZZ-LHS without NO_2 adsorption, the TDOS and band gap variation with strains are similar to those of As/Sb AC-LHS. In addition, after applying compressive strain to NO_2 -As/Sb ZZ-LHS, a new impurity state is generated in the range of 0–0.35 eV, and the Sb-p orbitals between the adsorbed NO_2 and LHSs exhibit strong orbital hybridization with the N-p and O-p orbitals, which corresponds to the maximum adsorption energy absolute value mentioned in Figure 2. For As/Sb ZZ-LHS, the change in TDOS before and after the adsorption of gas molecules under different strains is similar to As/Sb AC-LHS under no strain and tensile strain. It is worth noting that after the adsorption of NO_2 under compressive strain, the VBM of the system moves in the low-energy direction, and the CBM moves in the high-energy direction, resulting in a large band gap and a new state near the Fermi level. However, the TDOS of all LHSs under tensile strain did not significantly change before and after NO_2 adsorption, which proves the weak interaction between NO_2 and LHSs under tensile strain.

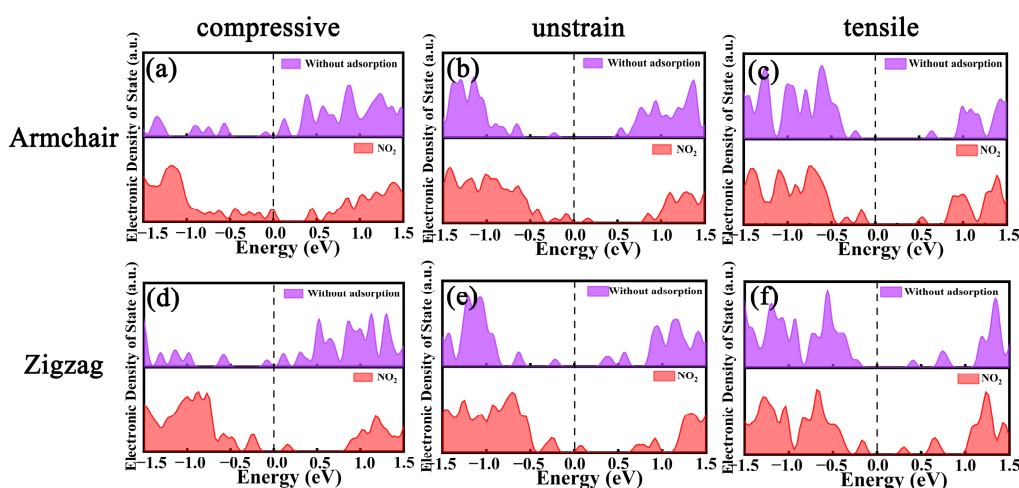


Figure 4. (a–c) Total density of armchair As/Sb LHS with and without NO_2 adsorption, (a) compressive strain, (b) unstrained and (c) tensile strain; (d–f) zigzag As/Sb LHS without NO_2 adsorption and adsorption TDOS at NO_2 , (d) compressive strain, (e) unstrained and (f) tensile strain.

Figure 5 displays all adsorption systems' partial density of states (PDOS). Figure S2a–c show the PDOS of As/Sb AC-LHS without NO_2 adsorption. The Sb-p orbital contributes significantly to the energy band under no strain and compressive strain. Under tensile strain, the VBM is mainly affected by the Sb-p orbital and the CBM is mainly affected by the As-p orbital. When no strain is applied, as shown in Figure 5b, the Sb-p orbital of VBM moves in the high energy direction, and the band gap reduces. When the compressive strain is applied, as shown in Figure 5a, the contribution of Sb-p orbitals to NO_2 -As/Sb AC-LHS are enhanced, and the As-p and Sb-p orbitals of VBM move in the high-energy direction, resulting in the electron DOS crossing the Fermi level and showing metallicity. After tensile strain is applied, as shown in Figure 5c, the Sb-p of VBM moves in the high-energy direction, and the As-p of CBM moves in the low-energy direction, resulting in a smaller band gap. For the As/Sb ZZ-LHS, the VBM is mainly contributed by the Sb-p orbital and CBM is mainly contributed by the As-p orbital under different strain conditions, as shown in Figure S2d–f. Adsorbing NO_2 does not alter the band structure, and the change in band gap is similar to that observed at the AC interface when no strain and tensile strain are applied. After applying compressive strain, the contribution of the Sb-p orbital to

the band gap is enhanced, and the As-p of CBM shifts towards the high-energy direction, leading to a larger band gap, as shown in Figure 5d. In addition, after NO₂ adsorption, the contributions of N-p and O-p orbitals to the Fermi level are mainly in the range of -0.5 eV and 0.3 eV, which does not affect the CBM or VBM of the system.

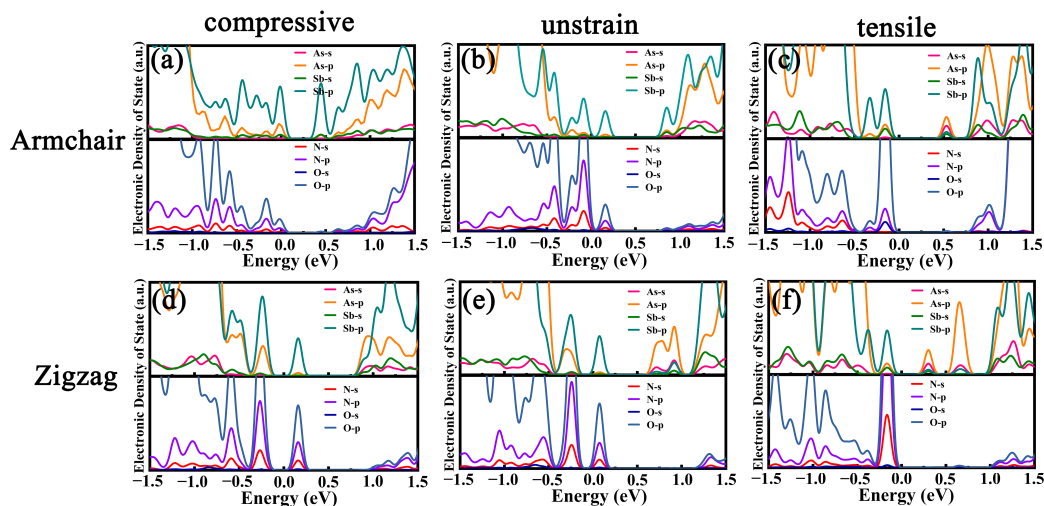


Figure 5. (a–c) Partial density of states of armchair As/Sb LHS-adsorbed NO₂ under (a) -4% compressive strain, (b) unstrained and (c) 4% tensile strain; (d–f) PDOS of zigzag As/Sb LHS-adsorbed NO₂ under (d) -4% compressive strain, (e) unstrained and (f) 4% tensile strain.

4. Conclusions

In summary, we constructed two LHSs based on As and Sb atoms along the AC and ZZ interfaces, and calculated their gas sensitivity for NO₂ gas under the strain conditions of -4% , 0% and 4% using the first principle calculation method. The results show that the adsorption effect of LHSs on NO₂ is stronger under compressive strain. Among them, As/Sb ZZ-LHSs have the largest adsorption energy of 2.79 eV, and exhibit a significant work function change before and after adsorption under compressive strain, indicating the highest sensitivity to NO₂. In addition, from TDOS, it can be seen that the electronic density of states in the valence band undergoes significant changes before and after adsorption. It is also worth mentioning that through PDOS, a new state has been discovered near the Fermi level, and the Sb-p orbitals have strong orbital hybridization with N-p and O-p orbitals. Due to these superior characteristics, the As/Sb LHSs with a ZZ interface under compressive strain may be an excellent candidate material for use as gas sensors for detecting NO₂ gas.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/cryst13091325/s1>. Figure S1: Top and side views of AC-LHS and ZZ-LHS at each strain node (-4% , 0% , 4%) when NO₂ is not adsorbed; Figure S2: PDOS of AC-LHS and ZZ-LHS without NO₂ adsorption.

Author Contributions: Conceptualization, H.Y., Y.Z., X.C. and J.L.; resources, D.F.; supervision, D.W. and X.F.; writing—original draft, L.Y. All authors have read and agreed to the published version of the manuscript.

Funding: This work was supported by the National Natural Science Foundation of China (62074018, 62174015 and 62275032), the Developing Project of Science and Technology of Jilin Province (20230508053RC and 20210509061RQ), and the Natural Science Foundation of Jilin Province (20210101473JC, 20210101150JC).

Data Availability Statement: The data that support the findings of this study are available from the corresponding authors upon reasonable request.

Conflicts of Interest: The authors declare no conflict of interest.

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