Gas-Sensing Properties of the SiC Monolayer and Bilayer: A Density Functional Theory Study

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ABSTRACT: Using density functional theory calculations, the adsorption of gaseous molecules (NO, NO₂, NH₃, SO₂, CO, HCN, O₂, H₂, N₂, CO₂, and H₂O) on the graphitic SiC monolayer and bilayer has been investigated to explore the possibilities in gas sensors for NO, NO₂, and NH₃ detection. The strong adsorption of NO₁ and SO₂ on the SiC monolayer precludes its applications in nitride gas sensors. The nitride gases (NO, NO₂, and NH₃) are chemisorbed on the SiC bilayer with moderate adsorption energies and apparent charge transfer, while the other molecules are all physisorbed. Further, the bilayer can effectively weaken the adsorption strength of NO₁ and SO₂ molecules, that is, NO₂ molecules are only weakly chemisorbed on the SiC bilayer with an E_ads of -0.62 eV, while SO₂ are physisorbed on the bilayer. These results indicate that the SiC bilayer can serve as a gas sensor to detect NO, NO₂, and NH₃ gases with excellent performance (high sensitivity, high selectivity, and rapid recovery time). Moreover, compared with other molecular adsorptions, the adsorption of NH₃ molecules significantly changes the work function of the SiC monolayer and bilayer, indicating that they can be used as optical gas sensors for NH₃ detection.

1. INTRODUCTION

Sensing gas molecules is critically important to environmental monitoring, space missions, control of chemical processes, and medical and agricultural applications. In particular, nitride gases such as NO, NO₂, and NH₃ which are produced from the combustion of coal, chemical fuels, and plastics, and exhaust emissions of motor vehicles, are highly toxic to human beings and animals as they inhibit the consumption of oxygen by the body tissues. For example, lower concentrations of nitrogen oxides can cause symptoms such as pharynx discomfort, and dry cough and high concentrations can cause pulmonary fibrosis, while high concentrations of ammonia can cause tissue lysis and necrosis, and irritation of the skin and mucous membranes can cause cornea or skin burns. In addition, nitrogen oxides are the main cause of acid rain and photochemical smog. Therefore, gas sensors with high sensitivity performance (such as high sensitivity and selectivity, rapid recovery time) to detect these gas molecules (NO, NO₂, and NH₃) are highly desired. In this context, designing and finding new gas-sensing materials with high performance have attracted considerable attention.

Two-dimensional (2D) nanomaterials have taken the forefront in innovative applications in gas sensors in the past decade after the successful experimental exfoliation of graphene. This is because those 2D nanomaterials have advantages such as large specific surface area, high carrier mobility, strong gas adsorption capacity under the condition of limited size, which can adsorb more gas molecules, and the associated charge transfer between gas molecules and the substrates. Recently, monolayer or few-layer 2D silicon carbide (SiC), which can be depicted simply as silicene/graphene, in which half or part of the atoms are replaced by the chemically similar C/Si atoms, were theoretical predictions and successful fabrication in the design of emerging electronic devices such as field effect transistors, lithium battery, and gas sensors. Previous studies have shown that 2D SiC have a nonbuckled honeycomb structure similar to graphene and have high thermodynamic and mechanical stability and semiconducting properties with wide band gaps, especially for stoichiometric graphite SiC monolayers and bilayers. Although the Si–C bonds of 2D graphitic-like SiC prefer sp² hybridization, Si atoms have more adsorption sites than C atoms, and thus make their adsorption activities increase. Previous studies have demonstrated that graphite SiₓCᵧ monolayers (also known as siligraphene or g-SiCₓᵧ) can be viewed as gas sensors for air pollutants. For example, Dong et al. have demonstrated that the SiCₓ (for short) is superior to Si-doped graphene in gas-sensing, enabling g-SiCₓ to be a promising material as a gas sensor for detecting NO, HCHO, or SO₂ from air mixture, and recently,
Monolayers are direct-gap semiconductors (and bilayers. It is well known that stoichiometric graphite SiC with high sensitivity. Despite these studies, to our knowledge, no systematic theoretical work has been reported for the gas-sensing properties of stoichiometric graphite SiC monolayers and bilayers. It is expected that stoichiometric graphite SiC monolayers and bilayers are direct-gap semiconductors (\(E_g \approx 2.5 \text{ eV}\)), while the most stable SiC bilayer is a bernard-type hexagonal stack, in which Si (C) atoms of one layer are located on the top of C (Si) atoms of the other layer. Furthermore, Yaghoubi et al. confirmed that stoichiometric graphite SiC monolayers have highly unique anisotropic transmission characteristics, making them highly sensitive to environmental conditions, which shows that the SiC monolayer is suitable for gas sensors. Moreover, experimental and theoretical calculations have shown that SiC nanotubes, which can be formed using the rolls of silagraphene, can be used to detect gases such as HCN, NO\(_2\), O\(_2\), and CO\(_2\). Therefore, it is expected that stoichiometric 2D SiC monolayers and bilayers may have high gas-sensing properties to detect toxic gases, being promising candidates for highly sensitive gas sensors.

In this work, we employed first-principle calculations based on density functional theory (DFT) to accurately describe the adsorption behavior of the NO, NO\(_2\), and NH\(_3\) gases on the SiC monolayer and bilayer, and thus to explore the possibility of the SiC monolayer and bilayer as NO, NO\(_2\), and NH\(_3\) gas sensors. To have a systematic and comparable discussion, we also studied the adsorption of CO, CO\(_2\), HCN, N\(_2\), O\(_2\), H\(_2\)O, and SO\(_2\) gas molecules on 2D SiC monolayers and bilayers. Our results showed that the SiC monolayer can be used as a gas sensor to detect NO, and is suitable for the optical gas sensor for NH\(_3\) detection. The SiC bilayer is a promising candidate for gas sensors to detect NO, NO\(_2\), and NH\(_3\) gas molecules.

2. RESULTS AND DISCUSSION

2.1. Structural and Electronic Properties of the SiC Monolayer and Bilayer. First, we optimized the \(3 \times 3 \times 1\) supercells of the SiC monolayer and bilayer. The optimized most stable structures of the SiC monolayer and bilayer are shown in Figure 1a,b, respectively. For the SiC monolayer, the optimized lattice parameters are \(a = b = 3.07\ \text{Å}\), while for the SiC bilayer, the optimized lattice parameters are \(a = b = 3.09\ \text{Å}\) within the C−Si bond length of 1.78 Å, and the distance between the monolayers is 3.65 Å. These results of structural properties are consistent with the results of previous studies. Furthermore, the electronic properties of the SiC monolayer and bilayer were calculated, and the band structures and density of states (DOS) are also shown in Figure 1. We found the direct band gaps of 2.55 and 1.70 eV for the SiC monolayer and bilayer, respectively. The hybridization between C 2p and Si 3p states is reasonable for the interaction of Si and C atoms in the SiC monolayer and bilayer, and the sp-hybridization occurs much farther from the Fermi level, which is completely different from the case of SiC crystals, where the sp\(^2\)-hybridization is the main contribution. It is well known that the GGA functional underestimates the band gaps of semiconductors. The HSE06 functional predicted that the SiC monolayer and bilayer have a band gap of 3.46 and 2.54 eV, respectively, which is much larger than our PBEsol results. We noted that what we are more concerned about is the change of electronic properties of the considered systems before and after adsorption, which can help us to realize the gas-sensing properties of the considered systems.

2.2. Molecular Adsorption on the SiC Monolayer. In order to obtain the most stable configurations of molecular gases adsorption on the SiC monolayer, based on the symmetry and directionality of the SiC monolayer, we constructed a variety of adsorption models for gas molecules on the SiC monolayer. For example, for the adsorption of the NO molecule, we considered the adsorption sites of the SiC monolayer, such as each C or Si atom, the bridge site of each C−Si bond, the center of the six-membered rings, and also considered NO is vertical or parallel to the monolayer. After full optimization, we obtained the most stable structures of gas molecules adsorption on the SiC monolayer. As discussed below, we mainly took into account the adsorption energy, bond distances, and transferred charge to estimate the
chemical or physical adsorption. In general, there is a limit on the energy, that is, ~0.5 eV to differentiate chemisorption from physisorption.\textsuperscript{41} We note that the limit on the energy of ~0.5 eV has no constraints, that is, it is not relevant to the size of the supercell, the number of layers, and the size of gas molecules. Further, it has been successfully used to describe physisorption and chemisorption of molecules on different systems, such as molecules on SiC nanotubes and nanocages,\textsuperscript{37–40} and other semiconducting monolayers.\textsuperscript{42–51}

We first investigated the NO adsorption, which is shown in Figure 2, and the relevant results are listed in Table 1. The

![Figure 2](https://pubs.acs.org/journal/acsodf)

Figure 2. Optimized structures of the SiC monolayer with molecular adsorption: (a) NO-1; (b) NO-2; (c) NO2-1; (d) NO2-2; (e) NH3-1; (f) NH3-2. For each molecule adsorbed on the SiC monolayer, its isomeric structure is denoted as 1 and 2 in the order of decreasing stability. We only show the structure around the adsorbed molecule. The red, blue, and white balls are O, N, and H atoms, respectively.

Then, we investigated the NO\textsubscript{2} molecular adsorption. Two most stable structures of NO\textsubscript{2} molecules adsorbed on the SiC monolayer are shown in Figure 2c,d. The most stable structure of NO\textsubscript{2} on the SiC monolayer, in which the two O atoms of NO\textsubscript{2} point to two Si atoms of the monolayer, forming two Si–O bonds with a bond length of 1.90 Å, has an adsorption energy of ~0.93 eV. Similar to the NO adsorption, structural deformation occurs in the SiC monolayer because of the strong adsorption of NO\textsubscript{2}, while the bond length of the N–O bond in the NO\textsubscript{2} molecule changes from 1.20 Åin an isolated NO\textsubscript{2} molecule to 1.28 Å, and the O–N–O angle changes from 134.38 to 117.94\textdegree. In addition, there is a charge transfer of 0.091 e from the NO\textsubscript{2} molecule to the SiC monolayer. These results indicate that the NO\textsubscript{2} molecule is chemisorbed on the SiC monolayer with apparent adsorption energy and obvious charge transfer. We also found the second stable adsorption state, which is shown in Figure 2d, within an adsorption energy of ~0.56 eV, much lower in energy by 0.37 eV than the most stable structure. In this configuration, the N atom in NO\textsubscript{2} points to one Si atom to form a Si–N bond with a length of 1.97 Å. The N–O bond length in NO\textsubscript{2} changes from the 1.20 Åin isolated NO\textsubscript{2} to 1.23 Å, and the O–N–O angle changes from the 134.38 to 124.80\textdegree. Furthermore, there is a charge transfer of 0.220 e from the NO\textsubscript{2} molecule to the SiC monolayer, which is much larger than that of the most stable structure. Even so, the structure shown in Figure 2d is less stable than the structure shown in Figure 2c. This feature was also found in NO\textsubscript{2} adsorption on other 2D nanomaterials\textsuperscript{42,43} and SiC nanotubes.\textsuperscript{38} This may be because two O atoms in the NO\textsubscript{2} molecule bind with the substrate (forming two O–Si bonds, which have a bond energy of about 4.46 eV) to form a more stable structure than one N atom in NO\textsubscript{2} binding with the substrate (forming a N–Si bond, which has a bond energy of about 3.68 eV).

Similar to the case of the second stable structure of NO\textsubscript{2} adsorbed on the SiC monolayer, the N atom of the NH\textsubscript{3} molecule bonds with one Si atom of the SiC monolayer to form the most stable configuration of NH\textsubscript{3} adsorbed on the monolayer, which is shown in Figure 2e. This structure has an adsorption energy of ~0.76 eV. The adsorption of NH\textsubscript{3} molecule induces a charge transfer of 0.310 e from the SiC monolayer to the NH\textsubscript{3} molecule. These results indicate that the chemisorption of the NH\textsubscript{3} molecule on the monolayer. In addition, we also obtained the most stable physisorption state of the NH\textsubscript{3} molecule on the monolayer, as shown in Figure 2f, whose \(E_{\text{ads}}\) is ~0.14 eV. Compared with the chemisorption structure, the NH\textsubscript{3} molecule flips over about 180\textdegree, and locates on the top site of one Si atom, making the distance between

### Table 1. Adsorption Energy (\(E_{\text{ads}}\)), Adsorption Distance (\(D\)), Charge Transfer (\(Q\)), Band Energy Gap (\(E_{\text{g}}\)), Work Function (\(\Phi\)), Recovery Time (\(\tau\)), and Adsorption Energy With Dipole Correction (\(E_{\text{ads,d}}\)) of the Optimized Structures for NO, NO\textsubscript{2}, and NH\textsubscript{3} Molecules Adsorbed on the SiC Monolayer

| system | \(E_{\text{ads}}\) (eV) | \(D\) (Å)\textsuperscript{a} | \(Q\) (e)\textsuperscript{b} | \(E_{\text{g}}\) (eV) | \(\Phi\) (eV) | \(\tau\) (s) | \(E_{\text{ads,d}}\) (eV) |
|--------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| NO:1   | ~0.56           | 1.80 (O–Si) 1.53 (N–C) 1.96 (N–Si) | 0.096           | 0.55           | 5.17           | 2.67 \times 10^{-3} | ~0.55           |
| NO:2   | ~0.51           | 2.04 (N–Si)    | 0.016           | 0.88           | 5.09           | 3.82 \times 10^{-4} | ~0.50           |
| NO\textsubscript{2}:1 | ~0.93 | 1.90 (O–Si) 1.90 (O–Si) | ~0.091 | 0 | 5.52 | 4.53 \times 10^{-3} | ~0.93 |
| NO\textsubscript{2}:2 | ~0.56 | 1.97 (N–Si) | ~0.220 | 0 | 5.71 | 2.66 \times 10^{-3} | ~0.54 |
| NH\textsubscript{3}:1 | ~0.76 | 2.00 (N–Si) | 0.310 | 2.50 | 4.35 | 6.17 | ~0.73 |
| NH\textsubscript{3}:2 | ~0.14 | 2.98 | 0.003 | 2.57 | 5.25 | 2.25 \times 10^{-10} | ~0.15 |

\textsuperscript{a}\(D\) is defined as the bond length or the shortest distance between the molecule and the SiC surface. \textsuperscript{b}\(Q\) is defined as the total Hirshfeld charge on the molecule, and a negative value indicates that the charge is transferred from the adsorbed molecule to the SiC monolayer.
the Si atom and N atom in NH$_3$ to be 2.98 Å. The physisorption of NH$_3$ leads to a very small charge transfer (only 0.003 e) from the SiC monolayer to the NH$_3$ molecule, indicating little effect on the electronic properties of the SiC monolayer due to the physisorption of NH$_3$.

We further considered the interaction between other molecules (CO$_2$, H$_2$, N$_2$, O$_2$, H$_2$O, and SO$_2$) and the SiC monolayer. The most stable structures of molecules adsorbed on the SiC monolayer are shown in Figure 3, and the relevant results are given in Table 2. Among these molecular adsorptions, we found that the physisorption of CO$_2$, H$_2$, N$_2$, and O$_2$ molecules on the SiC monolayer due to the bit adsorption energy, little charge transfer, and the large distance between the molecule and monolayer. For the adsorption of the H$_2$O molecule, the adsorption energy is −0.36 eV, and the distance between the O atoms in H$_2$O and the Si atoms is about 2.10 Å. In addition, there is a charge of 0.180 e transferred from the monolayer to the H$_2$O molecule. These results indicate that the adsorption state of the H$_2$O molecule is between strong physisorption and weak chemisorption. The most stable configuration of the SO$_2$ molecule adsorbed on the SiC monolayer, as shown in Figure 3f, has an adsorption energy of −1.25 eV. Because of the strong adsorption of SO$_2$, the SiC monolayer occurs structurally distorted, that is, the C atom and Si atoms, which interact with the SO$_2$ molecule to form two O–Si bonds and one S–C bond with bond lengths of 1.83, 1.83, and 1.81 Å, respectively, are protruded out of the monolayer surface.

In addition, to have a better understanding of the adsorption behaviors of molecules on the monolayer, we also studied the band structures and DOS of molecules adsorbed on the SiC monolayer, which are shown in Figure 4. Comparing with the electronic properties of the pure SiC monolayer (Figure 1c,d), the total DOS of the molecule-monolayer system and the LDOS of the corresponding molecules show that there are three ways for molecule adsorption to modulate the electronic properties of the SiC monolayer. First, NO, O$_2$, and SO$_2$ molecule adsorption introduces impurity states in the band gap, thereby decreasing the original band gap, indicating that these molecule adsorptions modify the electronic properties of the SiC monolayer to some extent. Although the O$_2$ molecule is physisorbed on the SiC monolayer, very similar to the chemisorption of NO and SO$_2$, the physisorption of O$_2$ changed significantly the band structure of the SiC monolayer because of the induced magnetic moment in the O$_2$ molecule. This behavior was also found in O$_2$ physisorption on SiC nanotubes and other 2D nanomaterials. Second, the adsorption of NH$_3$, CO$_2$, H$_2$, N$_2$, and H$_2$O molecules do not introduce any impurity states into the band gaps and thus have little effect on the band gap widths of the SiC monolayer. Concretely, CO$_2$ and H$_2$ molecules produce fully occupied states into the valence bands, which are mainly far away from the Fermi level (located at about <−3.5 eV under the Fermi level), while NH$_3$, H$_2$O, and N$_2$ molecules give rise to some impurity states (located at >2.5 eV above the Fermi level) within the conduction bands. Finally, the NO$_2$ molecule adsorption induces unoccupied local states in the conduction bands, and more importantly, the Fermi level crosses these states. These results indicate that the semiconducting properties of the SiC monolayer transit into conducting properties after the NO$_2$ adsorption, obviously indicating that the adsorption of the NO$_2$ molecule can apparently enhance the conductance of the SiC monolayer. The feature of stabilizing the Fermi level into the conduction band by the impurity states of the studied molecules were also reported in other 2D nanomaterials which show high sensitivity for the studied molecules.

Next, we discussed the gas-sensing properties (mainly involving sensitivity, selectivity, and recovery time) of the SiC monolayer for nitride gas detection. The change in band gap widths of the SiC monolayer reflects the change in the conductivity, which can be described by the following formula

$$\sigma \propto \exp \left( -\frac{E_g}{2kT} \right)$$

where $\sigma$ is the electrical conductivity of the material, $k$ is the Boltzmann constant, $T$ is the thermodynamic temperature, and $E_g$ is the band gap. It is clear that the conductivity is proportional to the band gap. Therefore, we can calculate the change in the band gap to obtain the change in conductivity before and after adsorption, and then use the change in

![Figure 3. Top and side views of the most stable configurations of the SiC monolayer with molecular adsorption: (a) CO$_2$; (b) H$_2$; (c) N$_2$; (d) O$_2$; (e) H$_2$O; (f) SO$_2$. The distances are given in Å.](image-url)

| system  | $E_{ads}$ (eV) | $D$ (Å) | $Q$ (e) | $E_f$ (eV) | $\Phi$ (eV) | $\tau$ (s) | $E_{ads-d}$ (eV) |
|---------|----------------|--------|--------|-----------|-------------|----------|-----------------|
| CO$_2$  | −0.08          | 3.36   | −0.001 | 2.54      | 5.06        | 2.22 × 10$^{-11}$ | −0.08          |
| H$_2$   | −0.03          | 3.01   | −0.011 | 2.55      | 5.09        | 2.86 × 10$^{-12}$ | −0.02          |
| N$_2$   | −0.05          | 3.22   | 0.017  | 2.52      | 5.06        | 5.93 × 10$^{-12}$ | −0.04          |
| O$_2$   | −0.13          | 2.77   | −0.039 | 0.04      | 5.20        | 1.54 × 10$^{-10}$ | −0.13          |
| H$_2$O  | −0.36          | 2.10 (O–Si) | 0.180 | 2.53      | 4.73        | 1.14 × 10$^{-6}$ | −0.34          |
| SO$_2$  | −1.25          | 1.83 (O–Si) | 1.83 (O–Si) | 1.81 (S–C) | −0.024 | 1.92     | 5.06 | 1.09 × 10$^7$ | −1.25 |

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conductivity ($\sigma$) to evaluate the sensitivity.\textsuperscript{48,49} For the adsorption of NO molecules, the band gap of the SiC monolayer changed from 2.55 to 0.55 eV, resulting in the conductivity changing significantly. For the adsorption of NO$_2$ molecules, the band gap of the SiC monolayer changed from 2.55 eV to 0, that is, the adsorption of NO$_2$ molecules led to the semiconductor properties of the SiC monolayer to conductor properties, resulting in a huge change in conductivity, which is consistent with the analysis of DOS. The NH$_3$ adsorption just resulted in a change in the band gap of 0.054 eV, which may indicate that the sensitivity of the SiC monolayer for NH$_3$ detection is low. However, we found that the transferred charge (0.310 e) between the NH$_3$ molecule and the SiC monolayer is relatively remarkable, which would lead to the changes of the electronic conductivity of the monolayer,\textsuperscript{12,48\textsuperscript{–}51} exhibiting high sensitivity to NH$_3$ gas. For the adsorption of SO$_2$ molecules, the band gap of the SiC monolayer is changed from 2.55 to 1.92 eV, making the conductivity change obvious, while the adsorption of CO$_2$, H$_2$, N$_2$, and H$_2$O led to little changes in conductivity, indicating that they hardly modify the conductivity of the SiC monolayer. This further shows that the SiC monolayer has comparatively low selectivity for nitride gas detection. Further, the recovery time has been estimated by the following equation

$$\tau = \nu_0^{-1} e^{-E_{ads}/kT}$$

where $\nu_0$ is the attempted frequency of the molecule and $E_{ads}$ is the adsorption energy. The recovery time can be used to evaluate the reusability of gas sensors.\textsuperscript{52,53} We assumed that the attempted frequencies of all molecules involved in this

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**Figure 4.** Band structure and DOS of (a) NO, (b) NO$_2$, (c) NH$_3$, (d) CO$_2$, (e) H$_2$, (f) N$_2$, (g) O$_2$, (h) H$_2$O, and (i) SO$_2$ adsorption on the SiC monolayer. The LDOS of molecules is also given as Cyan-filled area under the DOS curve. The Fermi level is set to zero.

**Figure 5.** Top and side views of the most stable configurations of the SiC bilayer with molecular adsorption: (a) NO; (b) NO$_2$; (c) NH$_3$; (d) CO$_2$; (e) H$_2$; (f) N$_2$; (g) O$_2$; (h) H$_2$O; (i) SO$_2$; (j) CO; (k) HCN. The distances are given in Å.
We found that the recovery time of NO, NO2, and NH3 molecules is 2.67 ms, 4.53 × 103 s (1.26 h), and 6.17 s, respectively, which show that the SiC monolayer has rapid recovery time to ensure it serves as a reusable gas sensor with rapid recovery time for NO and NH3 gas detection; however, the long recovery time of the NO2 molecule limits the reuse of the SiC monolayer as a NO2 sensor. Further, the large SO2 adsorption energy corresponds to a considerable recovery time (>12 h), which in turn makes the desorption of SO2 gas very difficult. These results indicate that the presence of SO2 may further limit the uses of the SiC monolayer as gas sensors for nitride gas detection.

In addition, we calculated the work function of the gas molecules before and after molecule adsorption, and the relevant results are shown in Tables 1 and 2. As a result, the adsorption of other molecules hardly introduces changes in the work function of the monolayer. Thus, we can conclude that the SiC monolayer can be used as an optical gas sensor to detect NH3 molecules.

2.3. Molecular Adsorption on the SiC Bilayer. Because of the long recovery time of the SiC monolayer as a NO2 sensor and the strong chemisorption of SO2 molecules, which seriously hamper the SiC monolayer serving as a nitride gas sensor, we further investigated the adsorption behaviors and gas-sensing properties of molecules on the SiC bilayer. Only if the SO2 hardly affect the electronic properties of the SiC bilayer, indicating the quite low sensitivity and selectivity of the bilayer for SO2 gas, it can show high selectivity of the SiC bilayer for sensing nitride gases. The most stable configurations of molecules adsorbed on the SiC bilayer are shown in Figure 5, and the relevant data are given in Table 3. The adsorption energy of CO and HCN molecules on the SiC bilayer to explore the selectivity of the SiC bilayer, as previous work have demonstrated that SiC nanotubes and 2D materials were potential gas sensors for CO and HCN detection. The most stable structures are shown in Figure 5, and the relevant data are given in Table 3. The adsorption energy of CO and HCN molecules on the SiC bilayer is 0.12 and 0.11 eV, respectively, and the distance between the molecule and the SiC bilayer is more than 2.60 Å. There is also a little charge transferred from the molecule to the bilayer. We thus can conclude that these two molecules are physisorbed on the SiC bilayer. Furthermore, the molecular adsorption causes the gaps between the monolayers in the bilayer, being in the range of 3.40–2.46 Å, which may lead to the change in electronic properties of the SiC bilayer. We further investigated the electronic properties of the SiC bilayer with molecular adsorption. The band gap widths of the considered system are given in Table 3, and the DOSs of the most stable configurations of molecules adsorbed on the bilayer are shown in Figure 6. We found that the trend features of the change in electronic properties of the SiC bilayer as a consequence of molecules adsorption are completely consistent with that of the SiC monolayer, particularly on the DOS. For example, similar to the case of the O2 molecule adsorbed on the SiC monolayer, the physisorption of O2 leads to significant changes in band structures of the SiC bilayer. We noted that the band gap of the pure SiC bilayer is 1.70 eV, but the physisorption of CO2, H2, N2, H2O, CO, and HCN leads to the band gap decreasing to about 1.40–1.45 eV. To understand the obvious changes of the band gaps, we calculated changes in the band structures of the SiC bilayer with the decrease of the distances between monolayers, which are shown in Figure 7. It can be seen in Figure 7 that the band gaps of the pure SiC bilayer become narrow with the decrease of the distances between monolayers. The band gap changes into the range of 1.42–1.48 eV when the distance decreases to 3.45–3.40 Å. Therefore, we may conclude that the adsorption of CO2, H2, N2, H2O, CO, and HCN does not modify the band structures of the SiC bilayer, but the changes in structures of the bilayer play a decisive role in the modification of the band structures of the bilayer.

We then discussed the gas-sensing properties of the SiC bilayer. Similar to the cases of NO and NO2 adsorption on the SiC monolayer, the adsorption of the NO molecule makes the band gap of the SiC bilayer change from 1.70 to 0.79 eV, resulting in the conductivity change significantly, and the adsorption of the NO2 molecule makes the band gap of the

| Molecule | \( E_D \) (eV) | \( D \) (Å) | \( Q \) (e) | \( E_g \) (eV) | \( \Phi \) (eV) | \( T \) (s) |
|----------|----------------|----------|--------|-------------|----------|--------|
| NO       | -0.59          | 2.05     | 0.017  | 0.79        | 5.09     | 8.54 × 10^-3 |
| NO2      | -0.62          | 1.96     | -0.225 | 0           | 5.69     | 2.73 × 10^-2 |
| NH3      | -0.83          | 1.99     | 0.316  | 1.32        | 4.38     | 78.9   |
| CO       | -0.13          | 3.37     | -0.004 | 1.44        | 5.14     | 1.52 × 10^-10 |
| H2       | -0.08          | 3.01     | -0.026 | 1.44        | 5.17     | 2.22 × 10^-11 |
| N2       | -0.10          | 3.32     | 0.007  | 1.45        | 5.14     | 4.79 × 10^-11 |
| O2       | -0.22          | 2.69     | -0.040 | 0.49        | 5.28     | 5.06 × 10^-9  |
| H2O      | -0.42          | 2.08     | 0.183  | 1.38        | 4.79     | 1.16 × 10^-5  |
| SO2      | -0.29          | 2.83     | -0.097 | 1.36        | 5.33     | 7.61 × 10^-6  |
| CO       | -0.12          | 2.63     | 0.080  | 1.44        | 5.06     | 1.04 × 10^-10 |
| HCN      | -0.11          | 3.52     | 0.024  | 1.41        | 4.95     | 7.08 × 10^-11 |
SiC bilayer be from 1.70 eV to 0, indicating a transition from a semiconductor to a conductor. For the adsorption of the NH$_3$ molecule, the band gap of the SiC bilayer changes from 1.70 eV into 1.32 eV, which is significantly larger than that of the H$_2$, CO$_2$, N$_2$, H$_2$O, SO$_2$, CO, and HCN adsorption, where the influence on the band gaps is relatively small, indicating that they hardly enhance the conductivity of the bilayer. The band gap of the bilayer changes into 0.49 eV because of the adsorption of the O$_2$ molecule, very similar to the case of NO adsorption. These results indicate that the magnitudes of conductivity changes because the adsorption of NO, NO$_2$, and NH$_3$ molecules are much larger than those of other molecules, indicating that the SiC bilayer is highly selective to NO, NO$_2$, and NH$_3$. It can be seen from Table 3 that the adsorption energies of NO, NO$_2$, and NH$_3$ molecules are much larger than those of other molecules, indicating that the SiC bilayer is highly selective to NO, NO$_2$, and NH$_3$. As discussed, the adsorption strength of the NO$_2$ molecule on the bilayer is much weaker than the SiC monolayer, resulting in a recovery time of 27.3 ms. However, the SiC bilayer slightly enhances the adsorption ability to the NH$_3$ molecule, which leads to an energy increase of 0.07 eV, and then makes the recovery time increase to 78.9 s. In this regard, the SiC monolayer has much more rapid recovery time for NH$_3$ molecules than the SiC bilayer, in contrast to the NO$_2$ molecules. The work function ($\Phi$) of the SiC bilayer was 5.12 eV. From Table 3, we found that the change in $\Phi$ of the SiC bilayer due to the NH$_3$ adsorption is much larger than that because of other gas adsorption, which indicates that the SiC bilayer has promising optical gas-sensing properties for NH$_3$ detection, very similar to the case of the SiC monolayer. This further indicates that NH$_3$ can be distinguished from NO and NO$_2$ gases via measuring the work function. Overall, taking the adsorption states, adsorption energy, charge transfer, the change in electronic properties, and recovery time in consideration, these results show that the SiC bilayer as a gas sensor has high sensitivity and selectivity, and rapid recovery time for NO, NO$_2$, and NH$_3$ detection, and is better than the SiC monolayer.

3. CONCLUSIONS

Using density functional theory calculations, the adsorption of toxic nitride gas molecules (NO, NO$_2$, and NH$_3$) and other molecules (SO$_2$, CO, HCN, O$_2$, H$_2$, N$_2$, CO$_2$, and H$_2$O) on the graphitic SiC monolayer and bilayer have been investigated to explore the possibilities in gas sensors for NO, NO$_2$, and NH$_3$ detection. For the SiC monolayer, we found that NO, NO$_2$, NH$_3$, and SO$_2$ molecules on the SiC monolayer present dramatic changes, especially regarding their electric conductivities. Other gas molecules prefer to physically adsorb on the monolayer. However, the very strong adsorption of NO$_2$ and SO$_2$ on the SiC monolayer makes desorption difficult, which precludes its applications to nitride gas sensors. However, we found that the adsorption of the NH$_3$ molecule significantly changes the work function of the SiC monolayer,
indicating that the SiC monolayer should be an optical gas sensor for NH$_3$ detection. We further investigated the adsorption of molecules on the SiC bilayer. The nitride gases (NO, NO$_2$, and NH$_3$) are chemisorbed on the SiC bilayer with moderate adsorption energies and apparent charge transfer, while the other molecules are all physisorption. The bilayer can effectively weaken the adsorption strength of NO$_2$ and SO$_2$ molecules, that is, the NO$_2$ molecule are only weakly chemisorbed on the SiC bilayer with an $E_{\text{ads}}$ of $-0.62$ eV, while SO$_2$ are physisorbed on the bilayer. The trend features of the change in electronic properties of the SiC bilayer as a consequence of molecules adsorption are completely consistent with that of the SiC monolayer. These results indicate that the SiC bilayer can be used as a gas sensor to detect NO, NO$_2$, and NH$_3$ gases with excellent performance (high sensitivity, high selectivity, and rapid recovery time).

4. COMPUTATIONAL METHODS

All DFT calculations were carried out using Dmol$^3$ program package implemented in Materials Studio. The exchange–correlation energy functional was described using the PBEsol form. The correlation energy functional was described using generalized density functional seminuclear pseudopotential (DSPP) implemented to treat the core electrons. The Hirshfeld scheme was used to describe the charge contributions and charge transfer between molecules and 2D SiC. In the geometry optimization, the convergence tolerances of energy, maximum force, and displacement were $1.0 \times 10^{-6}$ Ha, 0.002 Ha/Å, and 0.005 Å, respectively. In addition, a real-space global orbital cutoff radius of 4.6 Å was chosen in all calculations. The Brillouin zone was sampled by $8 \times 8 \times 1$ special $k$-points using the Monkhorst–Pack scheme. To prevent interactions between the adjacent supercells, a minimum of 20 Å vacuum space was kept. We also considered the Perdew–Burke–Ernzerhof (PBE) exchange correlation function method with van der Waals (vdW) correction under the Grimme scheme. We found that the results of the GGA-PBEsol method are more reasonable than those obtained by the PBE + Grimme method for the investigation of the structural and electronic properties of the SiC monolayer and bilayer, which are completely in agreement with previous studies.

In order to evaluate the adsorption stability of gas molecules on 2D SiC, we define the adsorption energy ($E_{\text{ads}}$) as

$$E_{\text{ads}} = E_{\text{SiC/gas}} - E_{\text{SiC}} - E_{\text{gas}}$$

where $E_{\text{SiC/gas}}$ represents the total energy of the system with gas adsorption, $E_{\text{SiC}}$ represents the energy of the substrate, and $E_{\text{gas}}$ represents the energy of the molecule. The negative $E_{\text{ads}}$ indicates that the adsorption process is exothermic, showing that the structures after gas adsorption are chemically stable. Furthermore, because of some molecules considered in our work, we also considered the dipole correction in the calculations and calculated the adsorption of molecules on the SiC monolayer. The adsorption energies are listed in Tables 1 and 2, and we found that the dipole correction hardly affected the structural properties, adsorption energy, and charge transfer after molecules adsorption on the monolayer. Thus, we did not consider the dipole correction in the study.

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**Notes**

The authors declare no competing financial interest.

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