Two-Dimensional Tetragonal GaN as Potential Molecule Sensors for NO and NO$_2$ Detection: A First-Principle Study

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ABSTRACT: Properties of gas molecules (NO, NH$_3$, and NO$_2$) adsorbed on two-dimensional GaN with a tetragonal structure (T-GaN) are studied using first-principles methods. Adsorption energy, adsorption distance, Hirshfeld charge, electronic properties, electric conductivity, and recovery time are calculated. It is found that these three molecules are all chemisorbed on the T-GaN with reasonable adsorption energies and apparent charge transfer. The electronic properties of the T-GaN present dramatic changes after the adsorption of NO$_2$ and NO molecules, especially its electric conductivity, but NH$_3$ molecule hardly changes the electronic properties of the T-GaN. Furthermore, the recovery time of the T-GaN sensor at $T$ = 300 K is estimated to be quite short for NO$_2$ and NO but very long for NH$_3$. Moreover, the magnetic properties of the T-GaN are changed obviously due to the adsorption of NO (or NO$_2$) molecule. Therefore, we suggest that the T-GaN can be a prominent candidate for application as NO$_2$ and NO molecule sensors.

1. INTRODUCTION

Gas sensing devices are becoming increasingly mandatory for homeland security, medical and environmental monitoring, space exploration, automotive applications, and chemical process control. To meet these demands, the sensing properties (mainly including sensitivity, selectivity, stability, and speed) of gas sensors should be greatly improved, and these have awakened an enormous interest in the development and selection of optimal sensing materials.1−5 Two-dimensional (2D) nanomaterials have taken the front row in innovative applications of gas sensors in the recent years,6−12 particularly after the successful experimental synthesis of graphene.13 This is because the advantages of using nanomaterials with small size and dimension for gas sensing stem from the large surface-to-volume ratio, high specific surface area, and more surface active site. These favor the adsorption of gases on the sensor and can increase the sensitivity of the device because the interaction between the analytes and the sensing part is higher.

Group-III nitride gas sensing devices have been explored theoretically and experimentally for many years.14−34 and the sensing materials based on group-III nitride are mainly concentrated on thin films (or nanosheets),14−20 one-dimensional nanotubes,21−25 and nanowires,26−28 and nanoclusters (or nanoparticles)29−34 Gallium nitride (GaN), as one archetype of group-III nitride, has been envisioned as one of the most promising materials for next-generation technology. In particular, 2D GaN has been theoretically predicted35−41 and experimentally realized.42−44 It was reported that the 2D GaN nanomaterials have shown high thermal stability, large band gap (that means low electrical conductance), and high surface-to-volume ratio,35−41 indicating that 2D GaN have great advantage in the applications of gas sensors. Therefore, it is very interesting and important to study the feasibility of using 2D GaN as gas sensors. Hennig group has predicted the structural and electronic properties of 2D GaN materials and found that 2D GaN materials with a tetragonal structure (named as T-GaN) are more energetically favorable over other 2D GaN structures.37 Furthermore, they have theoretically identified suitable substrates for the growth of 2D GaN materials.36,37 Each Ga and N atom of the T-GaN, much different from the 3-fold coordinated planar or buckled hexagonal structure, is bonded to four neighboring N and Ga atoms, respectively. Recently, new methods such as the migration-enhanced encapsulated growth method35,44 have been used for the synthesis of 2D GaN nanosheets. These new approaches may be applied to generate the T-GaN nanostructure. Polluting nitrogen components, such as NO, NO$_2$, and NH$_3$, are the byproduct of various chemical and biological processes and considered to be hazardous. Therefore, in this work, we employ first-principles calculations...
Figure 1. (a) Top and (b) side view for the optimized structure of the T-GaN, in which the alternating atoms are located in two different planes. Blue and brown balls represent N and Ga atoms, respectively. (c) The band structure and (d) total and partial density of states (DOS’s) for the structure of T-GaN. The Fermi-level energy in (c, d) is marked by a green dashed line.

2. CALCULATION METHODS AND MODEL

All of our DFT calculations are carried out using the DMol³ program package implemented in Materials Studio. The exchange and correlation effects of the electrons are described by using the spin-polarized generalized gradient approximation of Perdew, Burke, and Ernzerhof (GGA-PBE) functional with van der Waals correction proposed by Tkatchenko and Scheffler method. The standard DNP basis sets and density-functional semicore pseudopotentials fitted to all-electron relativistic DFT results are selected to describe the electron–ion interaction. The self-consistent field calculations are done with a convergence criterion of 10⁻⁶ au on the energy and electron density. We optimize the geometric parameters without symmetry constraints, meanwhile we set convergence criterions of 10⁻⁵ au on the gradient and displacement and 10⁻³ au on the total energy in geometrical optimization. We use a 3 × 3 × 1 supercell under the periodic boundary condition on the x and y axes to model the infinite T-GaN. The Brillouin zone is sampled by 10 × 10 × 1 special k-points for using the Monkhorst–Pack scheme. To prevent interactions between the adjacent supercells, a minimum of 20 Å vacuum space is kept.

To evaluate the stability of molecule adsorption on the T-GaN, the adsorption energy (E_ads) is defined as

\[ E_{\text{ads}} = E_{\text{(gas–T-GaN)}} - E_{\text{(gas)}} - E_{\text{(T-GaN)}} \]

where \( E_{\text{(gas–T-GaN)}} \), \( E_{\text{(gas)}} \), and \( E_{\text{(T-GaN)}} \) represent the total energy with full relaxation for the gas molecule adsorbed on the T-GaN, the corresponding pristine T-GaN, and single gas molecule, respectively. With this definition, positive adsorption energy indicates that the adsorption is endothermic whereas the opposite indicates the exothermic process. The charge transfer between T-GaN and absorbed molecules is analyzed on the basis of Hirshfeld analysis. The reliability and accuracy of our methods used here for investigating the structures and electronic properties of GaN systems with gases adsorption have been confirmed by previous studies.

3. RESULTS AND DISCUSSION

3.1. Structure of the Pure T-GaN. First, we discuss the structural geometries of the pure T-GaN, and the optimized stable structure is shown in Figure 1a,b. In the T-GaN, alternating atoms are located in different planes. There are two different types of Ga–N bonds, one is located along \( a_1 \) direction, whose bond length is 2.046 Å, whereas the other is located along \( a_2 \) direction, whose bond length is 1.906 Å. The Bravais lattice vectors of the T-GaN are given with \( a_1 = a_2 = a \), which is 3.745 Å. The buckling displacement (i.e., the distance between two planes) is about 0.71 Å. These results are consistent with those reported in previous studies. Figure 1c,d shows the band structure and density of states (DOS’s) of the pure T-GaN, respectively. The pure T-GaN is predicted to be a semiconductor with a wide band gap, which is 1.883 eV. It is well known that the DFT-GGA method used here obviously underestimates the absolute band gaps of semiconductors; thus, the real band gap of the T-GaN should be larger than that of our theoretical result. The band gap predicted by HSE06 hybrid functional should be closer to that of the experimental data. However, as discussed below, what we focused on is mainly concerned on the change of band gaps. For different methods, the change of band gaps seems to be similar. From the analysis of density of states, it can be found that the valence bands near Fermi level are mainly dominated by the 3p atomic orbitals of Ga atoms and the 2p atomic orbitals of N atoms and the contribution of the other atomic orbitals to the valence bands is very small.

3.2. Adsorption of NO₂, NH₃, and NO on the T-GaN.

Second, we investigate the adsorption behavior and electronic properties of molecules on the T-GaN. To obtain the most stable configurations of each molecule adsorption on the T-GaN, we have considered as many as possible initial structures for each molecule adsorbed on the T-GaN. Specifically, all possible starting adsorption sites have been considered, namely, tops (including the Ga and N atom in upper and lower layers, respectively), hollow, and bridge (including Ga–N bonds in upper and lower layers and the junction between the upper and lower layers) sites. Meanwhile, for these positions, different molecular orientations were examined. For example, for NO molecule, we considered three possible orientations. The molecule axis was oriented parallel or perpendicular (with the O atom pointing up or down) with respect to the T-GaN. Each initial structure was fully relaxed. The most stable adsorption configurations of each molecular gas on the T-GaN are presented in Figure 2, and the corresponding results are summarized in Tables 1 and 2.

Then, we discuss the adsorption of NO₂ molecule on the T-GaN. For the most stable configuration of NO₂ on the T-GaN, as shown in Figure 2a, there is only one O atom bonded with a
Distance between the N (or O) Atom of Molecule and T-GaN Surface (\(d_{\text{N-O}}\)), the Angle of the NO2 Molecule (\(\alpha\)), and the Band Energy Gap (\(E_{\text{g}}\)) for the Configurations of NO2 Molecule Adsorption on the T-GaN Sheet

Table 1. Calculated Adsorption Energy (\(E_{\text{ads}}\)), Charge Transfer from the T-GaN to NO2 Molecule (\(E_{\text{T}}\)), the Distance between the N and O Atom of NO2 Molecule (\(d_{\text{N-O}}\)), the Angle of the NO2 Molecule (\(\alpha\)), the Distance between the N (or O) Atom of NO2 and T-GaN Surface (\(d_{\text{N-G}}\)), and the Band Energy Gap (\(E_{\text{g}}\)) for the Configurations of NO2 Molecule Adsorption on the T-GaN Sheet

| System | \(E_{\text{ads}}\) (eV) | \(E_{\text{T}}\) (e) | \(d_{\text{N-O}}\) (Å) | \(\alpha\) (deg) | \(d_{\text{N-G}}\) (Å) | \(E_{\text{g}}\) (eV) |
|--------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| NO2-1  | −0.673          | −0.108          | 1.274 (1.215)   | 122.1           | 2.066           | 0.238           |
| NO2-2  | −0.644          | −0.136          | 1.228           | 127.5           | 2.135           | 0.122           |
| NO2-3  | −0.625          | −0.266          | 1.341           | 123.9           | 1.381           | 0.667           |

Table 2. Calculated Adsorption Energy (\(E_{\text{ads}}\)), Charge Transfer from the T-GaN to each Molecule (\(E_{\text{T}}\)), the Distance between the N and H (or O) Atom of the NH3 (or NO) Molecule (\(d_{\text{N-H}}\) or \(d_{\text{N-O}}\)), the Angle of H−N−H for the NH3 Molecule (\(\alpha\)), the Distance between the N (or O) Atom of Molecule and T-GaN Surface (\(d_{\text{N-G}}\)), and the Band Energy Gap (\(E_{\text{g}}\)) for the Configurations of NH3 and NO Molecule Adsorption on the T-GaN Sheet

| System | \(E_{\text{ads}}\) (eV) | \(E_{\text{T}}\) (e) | \(d_{\text{N-H}}\) (Å) | \(\alpha\) (deg) | \(d_{\text{N-G}}\) (Å) | \(E_{\text{g}}\) (eV) |
|--------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| NH3    | −1.317          | 0.289           | \(d_{\text{N-H}} = 1.023\) | 110.2           | 2.089           | 1.880           |
| NO-1   | −0.872          | −0.271          | \(d_{\text{N-O}} = 1.357\) | 1.890/1.374      | 0.080           |
| NO-2   | −0.661          | −0.033          | \(d_{\text{N-O}} = 1.174\) | 2.192           | 1.059           |

“Distance between the N atom and the O atom bonded with the Ga atom is 1.274 Å, whereas the other is 1.215 Å.”

Ga atom and the Ga−O bond length is 2.066 Å, which is consistent with that of Ga−O chemical bonds in Ga2O3 crystal, indicating the NO2 molecule is chemisorbed on the T-GaN. The chemisorption feature is further inferred from the adsorption energy, which is −0.673 eV. This is similar to the case of NO2 adsorbed on the GaN nanotubes,15 nanowires,16 and clusters.15 A charge transfer of 0.108e from the NO2 molecule to the T-GaN is found when one O atom is bonded with the T-GaN. For the pure NO2 molecule, the N−O bond length is 1.209 Å and the angle of O−N−O is 133.5°. After the adsorption, for the NO2 molecule, the distance between the N atom and the O atom bonded with the Ga atom is 1.274 Å and the other N−O bond length is 1.215 Å. The angle of O−N−O reduces to 122.1°. These results indicate that the NO2 molecule has an obvious deformation because of the adsorption, especially for the N−O bond, which is close to the Ga−O bond. We also obtained other lowest-energy structures of NO2 molecule on the T-GaN. For the second stable one, as shown in Figure 2b, it is found that the N atom in NO2 is bonded with a Ga atom in T-GaN, with the Ga−N bond length of 2.135 Å. The adsorption energy of this configuration is −0.644 eV, just higher than 0.029 eV from that of the most stable one. Meanwhile, we also found that the N atom in NO2 can bind to a N atom in T-GaN, forming a N−N bond with the bond length of 1.381 Å. This is the third stable configuration, as shown in Figure 2c. Its adsorption energy is −0.625 eV, only higher by 0.048 eV than that of the most stable one. Because of such a small energy difference between the three configurations of NO2 on T-GaN, it can be suggested that these adsorption states would occur when lots of NO2 molecules are close to the T-GaN. From Table 1, it can be seen that there are obvious charge transfers from the NO2 molecule to the T-GaN no matter what the interaction between NO2 molecule and the T-GaN is, indicating NO2 has electron-withdrawing capability.

Because the NH3 molecule is more complex than NO2, the number of initial structures of NH3 molecule on the T-GaN we set up were more than that of NO2 on the T-GaN. However, after full optimization of these initial structures, they have been changed into one structure, which is shown in Figure 2d. In the optimized structure of NH3 molecule on the T-GaN, the N atom of NH3 is bonded with a Ga atom, forming a Ga−N bond, whose length is 2.089 Å. The H−N distance is 1.023 Å and the angle of H−N−H is 110.2° for the NH3 after adsorption, which basically agree with those of the isolated NH3 molecule. It indicates that the adsorption does not influence the structure of the NH3 molecule. Meanwhile, the T-GaN also is not influenced by the adsorption, although the adsorption energy of the NH3 molecule on T-GaN is as large as −1.317 eV. Because of strong adsorption, NH3 molecule serves as an acceptor and withdraws 0.289e from the T-GaN.

Finally, we identify the structures of NO molecule on the T-GaN. The former two most stable structures of NO molecule on the T-GaN are shown in Figure 2e,f. For the most stable one, as shown in Figure 2e, whose adsorption energy is −0.872 eV, the O atom of NO is bonded with a Ga atom, whereas the N atom of NO is bonded with a N atom of the T-GaN, forming a Ga−O bond and a N−N bond, respectively. The Ga−O and N−N bond distances are 1.890 and 1.374 Å, respectively. Because of the NO adsorption, the T-GaN has an obvious deformation around the adsorption site. One Ga−N bond is

**Figure 2.** Optimized structures of T-GaN with gas molecule adsorption: (a−c) NO2; (d) NH3; (e, f) NO. We only show the structure around the adsorbed molecule. Isomeric structures for each molecule adsorbed on the T-GaN are labeled as 1, 2, and 3 in order of decreasing stability. Values in parentheses are relative energies in electron volts with respect to the most stable one for each species. Red and white balls are O and H atoms, respectively.
broken, and the distance is 2.483 Å, much larger than that of the pure T-GaN. Meanwhile, the N–O bond length in NO molecule is elongated from 1.164 Å in the isolated model to 1.357 Å. In the second stable configuration, as shown in Figure 2f, the N atom in NO binds to a Ga atom, thus forming a Ga–N bond. The Ga–N bond length is 2.192 Å, similar to that of Ga–N bonds in other GaN structures.\textsuperscript{52–54} Similar to the adsorption of NO\textsubscript{2} on the T-GaN, Hirshfeld charge analysis shows that there are apparent charge transfers from the NO\textsubscript{2} molecule to the T-GaN, indicating NO molecule plays a role as an electron-withdrawing functional molecule.

The calculated band structures and density of states (DOS’s) of the T-GaN with molecule adsorption are shown in Figures 3–5, respectively. All of the band gaps are listed in Tables 1 and 2. It is worth noting that although we have calculated the band structures and DOS of all of the structures, as shown in Figure 2, we just analyze the band structures and DOS of the most stable configurations for each molecule adsorbed on the T-GaN. Compared with the band structure of the pure T-GaN (Figure 1c), the band structures are modified obviously after the adsorption of NO and NO\textsubscript{2} molecules but the band structure, especially near the Fermi level, is not changed apparently because of the NH\textsubscript{3} molecule adsorption. This indicates that the NO and NO\textsubscript{2} adsorption greatly changes the electronic properties of the T-GaN. From Figure 2 and Tables 1 and 2, it can be seen that different orientations of NO\textsubscript{2} (or NO) molecule on the T-GaN result in different configurations of molecule/T-GaN systems and these configurations have quite different band structures. This may indicate that the surface polarity and configuration would play an important role in NO\textsubscript{2} and NO gas sensing of the T-GaN. Furthermore, comparing with the DOS of the pure T-GaN (Figure 1d), the total DOS of the molecule–T-GaN systems and the local density of states (LDOS’s) of the corresponding molecules.
show that these molecules modulate the electronic properties of the T-GaN in different manners: first, the adsorption of NO₂ molecule introduces certain impurity states in the band gap and the Fermi level crosses these states. Thus, the adsorption of NO₂ molecule would decrease the original band gap. Second, the analysis of LDOS shows that NH₃ molecule adsorption introduces fully occupied states that are strongly hybridized with the original states of T-GaN in the valence band and these states are nonlocalized. These results indicate that the interaction between the NH₃ molecule and the T-GaN is very strong, which is consistent with the analysis of adsorption energy. The Fermi level is pinned in the top of the valence band, same as the case of the pure T-GaN, indicating that the adsorption of NH₃ molecule does not change the band structure near the Fermi level of pure T-GaN. Third, the NO molecule adsorption induces unoccupied local states in the conduction band and more importantly, the Fermi level is shifted into original conduction bands, obviously indicating that the NO molecule adsorption can apparently enhance the conductance of the T-GaN.

3.3. Possibility of the T-GaN as a Gas Sensor. Next, we examine that whether the T-GaN be suitable as a molecular sensor for NO₂, NH₃, and NO detection. As mentioned above, these three molecules are all chemically adsorbed on the T-GaN with apparent $E_{\text{ads}}$ and have obvious charge transfers that may affect the electrical conductivity of the T-GaN. In this regard, the T-GaN can be viewed as a molecular sensor for NO₂, NH₃, and NO gas detection. However, the sensitivity of a good sensor should be of concern. The sensitivity can be evaluated by estimating the electric conductivity change of the T-GaN before and after adsorption, which relates to the band gaps ($E_g$) as follows:

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

where $\sigma$ is the electric conductivity of the configurations, $k$ is the Boltzmann constant ($k = 8.62 \times 10^{-5} \text{eV/K}$), and $T$ is the thermodynamic temperature. We found that the change of band gaps for the most stable structures of NO₂ and NO molecule adsorbed on the T-GaN is 1.645 and 1.803 eV, with respect to the corresponding pure T-GaN, respectively. Therefore, the NO₂ and NO molecules can be detected by calculating the conductivity change in the T-GaN before and after the adsorption process, in particular for NO molecule. However, the band gap energies of the T-GaN sheet are barely influenced by the adsorption of NH₃ molecule. These results are consistent with the analysis of band structures and DOS, especially for the NO. Although the adsorption of NH₃ molecule could hardly affect the electronic properties of the T-GaN, the adsorption-induced charge transfer between the NH₃ molecule and T-GaN, as mentioned above, is expected to affect the resistivity of the system, which would be measured experimentally and could be a maker for gas sensors. This should be similar to the cases of NH₃ molecule on monolayer MOS₂, phosphorene, and Ti₂CO₂. In these systems, the resistivities increase obviously due to the charge transfer induced by the adsorption of NH₃ molecule, although the adsorption of NH₃ molecule hardly changes the band structures of the systems. However, as discussed below, it is found that the T-GaN is still not suitable for NH₃ detection because of the recovery time.

Furthermore, it needs to be noted that the strong adsorption of a molecule on the T-GaN indicates that desorption of this molecule from the T-GaN could be quite complicated, that is to say, it may require a long recovery time. For a good sensor, the recovery time should be very short to satisfy the demand of sustainable use. Therefore, we then estimate the recovery time ($\tau$) of the considered molecules adsorbed on the T-GaN. The recovery time, using transition state theory, relates to the adsorption energy ($E_{\text{ads}}$) as follows:

$$\tau \propto \exp \left(\frac{E_{\text{ads}}}{kT}\right)$$

Figure 5. Total density of states (DOS’s) of the structures of the T-GaN with NO₂, NH₃, and NO. The Fermi-level energy is marked by vertical dashed line. The LDOS of corresponding gas molecules is also plotted by green lines. The positive and negative values represent spin-up and spin-down states, respectively.
\[ \tau = \nu_0^{-1} e^{-E_{ads}/kT} \]

where \( \nu_0 \) is the attempt frequency, \( k \) is the Boltzmann constant, and \( T \) is the temperature. Supposing the NH\(_3\) and NO molecules have the same order of magnitude for the attempt frequency as that of NO\(_2\) (\( \nu_0 = 10^{12} \text{ s}^{-1} \)), the recovery time of the T-GaN sensor at \( T = 300 \text{ K} \) is estimated to be 0.2 s, 3.6 x 10\(^4\) h, and 7.3 min for the adsorption energy of \(-0.673 \text{ eV} \) (NO\(_2\)), \(-1.317 \text{ eV} \) (NH\(_3\)), and \(-0.872 \text{ eV} \) (NO), respectively. The recovery time for NH\(_3\) is so long that it precludes the applications of the T-GaN as a reusable molecular sensor for NH\(_3\) gas, further indicating that the T-GaN is not suitable as a molecular sensor for NH\(_3\) detection.

Taking aspects such as adsorption energies, forms of adsorption (chemically or physically), charge transfer, the change of band structures and DOS, the change of conductivity, and recovery time into consideration, the T-GaN should be a promising reusable molecular sensor for highly sensitive NO\(_2\) and NO detection with a short recovery time. In fact, this perspective can be concluded by using a completely new transduction principle, which is the exploitation of magnetic instead of electrical property modifications due to surface–gas interaction in the active material.\(^{61,62}\) Our results show that the pure T-GaN is nonmagnetic. The adsorption of NO (or NO\(_2\)) molecule introduces spin polarization in the T-GaN with a magnetic moment of approximately 1 \( \mu_B \), indicating that magnetic properties of the T-GaN are changed obviously due to the adsorption of NO (or NO\(_2\)) molecule, which is similar to the cases of NO (or NO\(_2\)) on GaN nanowires\(^{26}\) and nanocluster.\(^{26}\) However, the net spin polarization of the T-GaN is not modified due to the adsorption of NH\(_3\) molecule. In this regard of the change of magnetic properties, the T-GaN can be viewed as a highly sensitive gas detection technique based on the measurement of the local magnetic moment in the T-GaN using various experimental methods such as atomic force microscopy or superconducting quantum interference device magnetometry.\(^{63-65}\) To further investigate the origin and distribution of the magnetic moment, we calculated the magnetic moment of each atom in the molecule–T-GaN systems. The spin density of the most stable configurations of NO\(_2\) (or NO) adsorbed on the T-GaN is shown in Figure 6.

![Figure 6](image_url)

Figure 6. Spin density of the most stable configurations of (a) NO\(_2\) and (b) NO adsorption on the T-GaN with isovalues of ±0.005 e/Å\(^3\).

The magnetic moment is mainly located at the NO\(_2\) (or NO) molecule and the N atom of T-GaN that is closest to the NO\(_2\) (or NO) molecule and chiefly originates from the 2p states of N and O atoms.

Finally, it is interesting to compare our results with those of previous studies. To the best of our knowledge, there are just a few experimental and theoretical studies on the investigation of gas sensing materials based on pure GaN nanostructures to detect NO\(_x\), NO\(_2\), and NH\(_3\) gases. Bishop et al. have experimentally demonstrated that the GaN device, which is processed with 20 nm Pt on the n-type GaN sample, was not responsive to 15 ppm of either NO\(_2\) or NH\(_3\) because the concentration is below the detection limit of the device.\(^{20}\) Our results show that the T-GaN can even detect one NO\(_2\) molecule. Khan and Srivastava\(^{25}\) have predicted that the GaN nanotube shows high sensitivity to the adsorption of NO\(_2\) and NH\(_3\); however, the adsorption energy of NO\(_2\) and NH\(_3\) is in the range of 1.11–1.41 and 0.95–0.99 eV, respectively, indicating that the GaN nanotube would have much longer recovery time than that of the T-GaN. Recently, we have investigated the adsorption of gas molecules (SO\(_2\), NO\(_2\), HCN, NH\(_3\), H\(_2\)S, CO, NO, O\(_2\), H\(_2\), CO\(_2\), and H\(_2\)O) on the graphitic GaN sheet with an atomically flat planar honeycomb hexagonal structure (PL-GaN) using density functional theory calculations.\(^{60}\) It is found that the PL-GaN sheet should be a highly sensitive and selective NH\(_3\) sensor with a short recovery time. NO and NO\(_2\) molecules are physically adsorbed on the PL-GaN sheet. These results are very different from our present work, indicating that the T-GaN and PL-GaN have entirely different gas sensing properties.

4. CONCLUSIONS

In conclusion, using density functional theory calculations, the adsorption of nitrogen molecules (including NO\(_2\), NH\(_3\), and NO) on the 2D tetragonal GaN (T-GaN) has been investigated. It is found that these three molecules are all chemisorbed on the T-GaN with reasonable adsorption energies and apparent charge transfer. The electronic properties of the T-GaN sheet present dramatic changes after the adsorption of NO\(_2\) and NO molecules, especially their electric conductivity, but NH\(_3\) molecule hardly changes the electronic properties of the T-GaN. Meanwhile, the very strong adsorption of NH\(_3\) on the T-GaN makes its desorption difficult, which precludes its applications to NH\(_3\) sensors. Taking into consideration various aspects, such as the adsorption energies, charge transfer, the change of the electric conductivity, and the recovery time, it is concluded that the T-GaN can be viewed as a potential molecular sensor for NO\(_2\) and NO detection. Furthermore, the net spin polarization of the T-GaN is obviously changed into about 1 \( \mu_B \) after the adsorption of the NO (or NO\(_2\)) molecule, which indicates the T-GaN is a promising candidate for a highly sensitive magnetic sensor for detection of NO and NO\(_2\).

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The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This work was supported by grants from National Natural Science Foundation of China (Nos. 61774056, 11304080, and 11604080) and the Innovation Team of Henan University of Science and Technology (No. 2015XTD001).

DOI: 10.1021/acsomega.7b01586
ACS Omega 2017, 2, 8888–8895
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