Adsorption performance of M-doped (M = Ti and Cr) gallium nitride nanosheets towards SO$_2$ and NO$_2$: a DFT-D calculation

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The structure, adsorption characteristics, electronic properties, and charge transfer of SO$_2$ and NO$_2$ molecules on metal-doped gallium nitride nanosheets (M-GaNNS; M = Ti and Cr) were scrutinized at the Grimme-corrected PBE/double numerical plus polarization (DNP) level of theory. Two types, M$_{Ga}$-GaNNS and M$_{N}$-GaNNS, of doped nanostructures were found. The M$_{Ga}$ sites are more stable than the M$_{N}$ sites. The results showed that adsorption of SO$_2$ and NO$_2$ molecules on Ti$_{Ga,N}$-GaNNS is energetically more favorable than the corresponding C$_{Ga,N}$-GaNNS. The stability order of complexes is energetically predicted to be as NO$_2$-Ti$_{Ga}$-GaNNS > NO$_2$-T$_{N}$-GaNNS > SO$_2$-T$_{Ga}$-GaNNS > SO$_2$-T$_{N}$-GaNNS > NO$_2$-Cr$_{N}$-GaNNS > SO$_2$-Cr$_{Ga}$-GaNNS > SO$_2$-Cr$_{N}$-GaNNS > SO$_2$-Cr$_{Ga}$-GaNNS. The electron population analysis shows that charge is transferred from M$_{Ga}$,N-GaNNS to the adsorbed gases. The Ti$_{Ga}$-GaNNS is more sensitive than the other doped nanostructures to NO$_2$ and SO$_2$ gases. It is estimated that the sensitivity of Ti$_{Ga}$-GaNNS to NO$_2$ gas is more than to SO$_2$ gas.

1. Introduction

At present, air pollution is a significant factor limiting economic progressions. The emission of toxicant gases into the air is a serious matter due to the dangers of these air pollutants. The source of air pollutants might be extensive in the Earth’s environment. Sulfur dioxide (SO$_2$) and nitrogen dioxide (NO$_2$) are noteworthy gaseous pollutants, discharged from natural and industrial procedures which have major environmental effects. Thus, specific harmful gas detecting will be a major advantage to daily life for all people.

For the first time in 2005, boron nitride (BN) nanosheets were forecast. The honeycomb samples of BN sheets have analogies similar to graphene with equal numbers of alternating boron and nitrogen atoms that exhibit remarkable properties. The electronic properties of BN sheets can be modified by B or N vacancies, Stone–Wales defects and doping heteroatoms. In recent years, different studies have been done via surface quantum engineering of BN nanosheets. For BN modification, the doped BN nanosheets were explored for developing a sensor for detecting harmful gases.

Recently, III–V nanostructures have attracted great attention for their potential applications in novel electronic, optical, and electrochemical devices. One of the III–V nanostructures were gallium nitride nanosheets (GaNNSs) which have been theoretically predicted and then experimentally discovered. It was found that the GaNNSs have many remarkable properties such as a high surface area to volume ratio, high thermal stability and a tunable band gap indicating that GaNNSs have advantages in electronic usage such as effective gas sensor applications and so on. There are some experimental studies focusing on the GaN based NO$_2$ and SO$_2$ sensors. Bishop et al. suggested a double Schottky junction NO$_2$ gas sensor based on BGaN/GaN. Triet et al. synthesized Al$_{0.23}$Ga$_{0.77}$/N/GaN-based Schottky diode sensors for SO$_2$ gas detection. For example, the adsorption capabilities of gallium nitride nanosheets towards noxious gases (such as HCN, NH$_3$, H$_2$S, H$_2$, CO$_2$ and H$_2$O) have been described. Therefore, most of the research studies have focused on nanomaterials for increasing the adsorption of adsorbates on GaNNSs. For this purpose, the electronic properties of GaNNS can be modified by doping which generates more reactive adsorption sites. Transition metals such as Ti, Cr, Fe, Ni and Zn have been theoretically explored as dopants in GaNNSs to increase the adsorption properties towards CO harmful gases. The adsorption of H$_2$S, NH$_3$ and SO$_2$ molecules on pure and doped GaNNSs has been considered using first-principles calculations. The results show that the metal doped GaNNSs are more suitable for gas molecules detection compared with the pure ones. The doping effect of metal atoms on the electronic properties of GaNNSs was studied for tuning the opto-electronic properties, gas adsorption, hydrogen storage and catalytic reaction. The electronic and optical properties of GaNNSs as a function of thickness and strain with predictive calculations were scrutinized. Based on the results reported about the magnetic properties of GaNNSs, the metallic and
ferromagnetic properties of GaNNSs can be attained by semi-hydrogenation.\textsuperscript{25} The chemical oxidation of GaNNSs was explored by using first-principles calculations\textsuperscript{24} that show the oxygen adsorption mechanism can be useful for application in novel semiconducting materials. So, it would be attractive to continue investigating the promising applications of GaNNSs in gas sensors.

To the best of our knowledge, this is the first report on the adsorption of SO\textsubscript{2} and NO\textsubscript{2} molecules on the surface of Ti and Cr doped GaNNSs. The influence of transition metals doping on the adsorption behavior of SO\textsubscript{2} and NO\textsubscript{2} on the metal doped GaNNSs for exploring the possibility of using the doped GaNNSs as candidates for removing and sensing of these molecules was considered herein at the Grimme-corrected PBE/double numerical plus polarization (DNP) level of theory.

2. Computational details

In this theoretical research, the double numerical plus polarization (DNP) basis sets were selected implemented in the DMol\textsuperscript{3} package.\textsuperscript{55,56} The periodic spin-unrestricted DFT calculation is employed using generalized-gradient approximation (GGA) with the Perdew–Burke–Ernzerhof (PBE) functional.\textsuperscript{57} The density functional semi-core pseudopotentials (DSPP) were generated by fitting all-electron relativistic DFT results.\textsuperscript{38}

To consider the van der Waals (vdW) interactions, an empirical dispersion-corrected density functional theory (DFT-D) was used in the calculations. The Brillouin zone integration was sampled using a 10 × 10 × 1 Monkhorst-Pack grid. A convergence tolerance of energy of 1.0 × 10\textsuperscript{-5} Ha, maximum force of 0.001 Ha per Å, and maximum displacement of 0.005 Å were employed in all the geometry optimizations. To get reliable results, the real space global orbital cutoff radius was set as high as 5.2 Å and the smearing of electronic occupations to be 0.005 Ha.

To calculate the adsorption energies (AE) of the SO\textsubscript{2} and NO\textsubscript{2} molecules on the pure and metal doped GaNNSs, the following equation is given:

\[ AE = E_{\text{T}} - [E_S + E_m] \]  

(1)

where \( E_{\text{T}} \), \( E_S \), and \( E_m \) are the energies of gas-M-GaNNSs complexes, M-GaNNSs and SO\textsubscript{2} or NO\textsubscript{2} molecules, respectively.

3. Results and discussion

3.1. Adsorption of SO\textsubscript{2} and NO\textsubscript{2} gas molecules over pure GaNNSs

The optimized geometries of adsorbed molecules and gallium nitride nanosheets are displayed in Fig. 1. As demonstrated in Fig. 1, the calculated bond lengths of X=O (X = N and S) in free SO\textsubscript{2} and NO\textsubscript{2} molecules are 1.482 Å and 1.201 Å, respectively, and that of the Ga–N bond length in the optimized geometry of GaNNS is 1.861 Å.

To find the most stable complexes obtained from adsorption of SO\textsubscript{2} and NO\textsubscript{2} gas molecules on the GaNNS, several configurations of SO\textsubscript{2} and NO\textsubscript{2} molecules on top of the GaNNSs are explored. The most stable adsorption complexes are illustrated in Fig. 1. After optimization, the C\textsubscript{2} axis of the SO\textsubscript{2} molecule is parallel to the GaNNS and that of the NO\textsubscript{2} molecule is perpendicular to the nanosheet. As presented in Table 1, the nearest distances between the SO\textsubscript{2} and NO\textsubscript{2} molecules with SO\textsubscript{2}–GaNNS and NO\textsubscript{2}–GaNNS are 1.782 Å and 2.298 Å, respectively.

The values of the adsorption energies (AEs) are −27.22 and −11.86 kcal mol\textsuperscript{−1} for SO\textsubscript{2}–GaNNS and NO\textsubscript{2}–GaNNS complexes, in good agreement with the smaller SO\textsubscript{2}–GaNNS distance obtained. Hence, the SO\textsubscript{2} and NO\textsubscript{2} molecules are chemically adsorbed on the GaNNS. The adsorption energy for the SO\textsubscript{2} molecule on the GaNNS is comparable with those found for graphene (−6.45 kcal mol\textsuperscript{−1})\textsuperscript{39} and boron nitride nanosheet (−7.14 kcal mol\textsuperscript{−1})\textsuperscript{21} For adsorption of NO\textsubscript{2} on graphene, the calculated adsorption energy is −11.06 kcal mol\textsuperscript{−1}.\textsuperscript{41}

\begin{table}
\centering
\caption{The calculated adsorption energy (AE), equilibrium distance between molecules and nanosheet (D), charge of Ga and N atoms (Q), charge transfer (CT) and band gaps for the most stable adsorption complexes.}
\begin{tabular}{lllll}
\hline
Configurations & AE (kcal mol\textsuperscript{−1}) & D (Å) & Q (e) & CT (e) & Band gap (eV) \\
\hline
Pure GaNNS & — & — & 0.39\textsuperscript{Ga} (−0.39)\textsuperscript{N} & — & 2.52 \\
SO\textsubscript{2}–GaNNS & −27.22 & 1.782 & 0.40 (−0.38) & 0.17 & 2.51 \\
NO\textsubscript{2}–GaNNS & −11.86 & 2.298 & 0.39 (−0.39) & 0.09 & 0.29 \\
\hline
\end{tabular}
\end{table}

The Hirshfeld charges on the Ga and N atoms in pristine GaNNS are 0.39e and −0.39e, respectively, which change to 0.40e and −0.38e in SO\textsubscript{2}–GaNNS, and 0.39e and −0.39e in NO\textsubscript{2}–GaNNS. The charges on S and O change from 0.38e and −0.19e.
in free SO$_2$ to 0.33 $e$ and $-0.25e$ in SO$_2$-GaNNS, respectively. Besides, the charges on N and O are 0.17$e$ and $-0.09e$ which change to 0.11$e$ and $-0.10e$ in NO$_2$-GaNNS. This reveals that oxygen atoms in SO$_2$-GaNNS and NO$_2$-GaNNS complexes have the main contribution to charge transfer between the gas and nanosheet. The charge analyses show that the 0.17$e$ and 0.09$e$ charges are shifted from the GaNNSs to the SO$_2$ and NO$_2$ molecules, respectively, in good agreement with greater AE found for the SO$_2$-GaNNS complex.

The negative AE$s$ demonstrate the orbital interactions between the gases and GaNNS. The Mulliken electron populations of the total and each of the $s$, $p$ and $d$ orbitals before and after interactions are given in Table 2. Inspection of the $s$, $p$ and $d$ orbital contributions in the free gases and in the SO$_2$-GaNNS and NO$_2$-GaNNS complexes indicate that the $p$ orbital of the S atom in SO$_2$-GaNNS and O atom in NO$_2$-GaNNS have the most contribution in the interaction of molecules with the d orbital of Ga and p orbital of N atoms in the GaNNS. Comparison of the total electron population of orbitals shows that the population increases by 0.352$e$ for SO$_2$ and 0.169$e$ for NO$_2$ after interaction of the gas with the surface. This indicates that the adsorbates will get electrons from the GaNNSs. The change in the electronic population of the orbitals in SO$_2$-GaNNS is greater than for NO$_2$-GaNNS, in good agreement with the greater AE and Hirshfeld charge transfer values found for SO$_2$-GaNNS compared with NO$_2$-GaNNS.

### Table 2: Mulliken electron population of the total and each of the $s$, $p$ and $d$ orbitals before and after interactions

| Orbital | Total pop. | $s$ | $p$ | $d$ | Total pop. | $s$ | $p$ | $d$ |
|---------|------------|-----|-----|-----|------------|-----|-----|-----|
| Free SO$_2$ | | | | | NO$_2$-CrGa-GaNNS | | | |
| S | 15.558 | 5.838 | 8.872 | 0.848 | N | 6.72 | 3.637 | 2.942 | 0.14 |
| O | 8.22 | 3.836 | 4.346 | 0.04 | O | 8.346 | 3.839 | 4.461 | 0.047 |
| NO$_2$ | | | | | Cr | 13.317 | 2.592 | 6.454 | 4.272 |
| S | 15.514 | 5.674 | 8.922 | 0.918 | NO$_2$-Cr$_x$Ga$_{1-x}$GaNNS | | | |
| O | 8.424 | 3.846 | 4.546 | 0.032 | N | 6.799 | 3.851 | 4.272 | 0.055 |
| NO$_2$-GaNNS | | | | | O | 8.343 | 3.852 | 4.443 | 0.05 |
| N | 6.669 | 3.541 | 2.972 | 0.156 | Cr | 13.917 | 2.71 | 6.441 | 4.767 |
| O | 8.25 | 3.841 | 4.36 | 0.049 | SO$_2$-CrGa-GaNNS | | | |
| Ti$_{Ga}$-GaNNS | Ti | 11.244 | 2.658 | 6.202 | 2.384 | S | 16.613 | 5.802 | 9.203 | 0.608 |
| Ti$_{Cr}$-GaNNS | Ti | 11.465 | 2.612 | 6.347 | 2.505 | O | 8.364 | 3.834 | 4.499 | 0.031 |
| Cr$_{Ga}$-GaNNS | Ti | 11.465 | 2.612 | 6.347 | 2.505 | Ti | 11.018 | 2.433 | 6.304 | 2.281 |
| Cr$_{Cr}$-GaNNS | Cr | 13.357 | 2.655 | 6.345 | 4.357 | SO$_2$-Ti$_{Ga}$-GaNNS | | | |
| Cr$_{Cr}$-Ga$_{Ga}$ | Cr | 14.014 | 2.688 | 6.232 | 4.894 | S | 16.561 | 5.82 | 9.29 | 0.542 |
| NO$_2$-Ti$_{Ga}$-GaNNS | N | 6.72 | 3.644 | 2.932 | 0.142 | O | 8.399 | 3.837 | 4.531 | 0.03 |
| NO$_2$-Ti$_{Cr}$-GaNNS | Ti | 11.048 | 2.45 | 6.3 | 2.3 | Cr | 13.286 | 2.589 | 6.463 | 4.234 |
| N | 6.734 | 3.666 | 2.934 | 0.134 | S | 16.561 | 5.82 | 9.29 | 0.542 |
| O | 8.382 | 3.86 | 4.78 | 0.046 | O | 8.423 | 3.856 | 4.532 | 0.034 |
| Ti | 11.386 | 2.516 | 6.44 | 2.43 | Cr | 13.842 | 2.714 | 6.462 | 4.667 |

#### 3.2. Ti and Cr doped GaNNSs

In order to investigate the effect of metal doping on the geometrical and electronic properties of the GaNNS$s$s, one of the central atoms in the nanosheet was substituted by Ti and Cr metal atoms. Hereafter, $M_{Ga}$-GaNNS and $M_{Ga}$-GaNNS denote that Ga and N atoms in GaNNS have been substituted by M metal atoms, respectively.

The optimized structures of $M_{Ga}$-GaNNSs are illustrated in Fig. 2. The average bond distances between the metal atoms and the neighboring atoms are given in Table 3. The results show that the M-Ga bonds in $M_{Ga}$- GaNNS nanostructures are longer than the M-N bonds in $M_{Ga}$-GaNNSs. For example, the Ti-Ga and Cr-Ga bonds are longer than the Ti-N and Cr-N bonds by about 0.92 and 0.62 Å, respectively. Accordingly, it is predicted that binding of the metal to the nanosheet is stronger for $M_{Ga}$-GaNNS than $M_{Ga}$-GaNNS. Fig. 2 presents the three bond angles $A_1$, $A_2$ and $A_3$ around the M atoms of the NS and their average values are listed in Table 3. The averages of the three bond angles are $120.0^\circ$, $119.9^\circ$, $83.1^\circ$ and $87.1^\circ$ in Ti$_{Ga}$-GaNNS, Cr$_{Ga}$-GaNNS, Ti$_{Cr}$-GaNNS and Cr$_{Cr}$-GaNNS, respectively.

The binding energies (BE$s$s) of Ti$_{Ga}$-GaNNS, Ti$_{Cr}$-GaNNS, Cr$_{Ga}$-GaNNS and Cr$_{Cr}$-Ga$_{Ga}$ are $-330.5$, $-236.1$, $-246.9$ and $-61.6$ kcal mol$^{-1}$, respectively (Table 3). It is found that the BE$s$s increase in the order $M_{Ga}$-GaNNSs $>$ $M_{Ga}$-GaNNSs so that the value for the Ti$_{Ga}$-GaNNS structure is greater than other ones. Therefore, the Ga sites for M doping are energetically more appropriate...
than N sites. The sequence of BEs for the \( M_{Ga-N-GaNSs} \) series is \( Ti \) > \( Cr \), and that of the \( M_{N-GaNSs} \) series is \( Ti \) > \( Cr \). The more negative BE indicates that the adatom is easier to be incorporated into the \( GaNSs \) and M doped \( GaNSs \) are stable.

The Hirshfeld\textsuperscript{44} charge values of M atoms for \( M-GaNSs \) are shown in Table 3. The results show that the charge of the M atom in all M-doped \( GaNSs \) is positive, indicating that the \( GaNSs \) in many cases acts as an electron-withdrawing support. The considerable electron transfer from the metal atom to the \( GaNSs \) leads to the strong bonding between the M atom and its neighbor atoms and stabilization of single-metadoped \( GaNSs \).

Fig. 2 Optimized geometries of Ti and Cr doped \( GaNSs \).

Table 3 The calculated average of M–N and M–Ga bond distances, average of bond angles (\( A_1, A_2 \) and \( A_3 \)), binding energies of pristine and M (M = Ti and Cr) doped \( GaNSs \) and Hirshfeld charge values of M atoms

| Configurations | Bond distances (Å) | Bond angle (°) | Binding energies (kcal mol\(^{-1}\)) | Q (e) |
|----------------|-------------------|---------------|-------------------------------|-------|
| GaNSs          | 1.862             | 118.2         | —                             | —     |
| Ti\textsubscript{Ga}-GaNSs | 2.913             | 120.0         | —330.5                      | 0.30  |
| Ti\textsubscript{Ga}-GaNSs | 2.838             | 83.1          | —236.1                      | 0.26  |
| Cr\textsubscript{Ga}-GaNSs | 1.883             | 119.9         | —246.9                      | 0.43  |
| Cr\textsubscript{Ga}-GaNSs | 2.505             | 87.1          | —61.6                       | 0.28  |

The range of adsorption energies for \( SO_2 \) and \( NO_2 \) adsorbed on Ti-doped \( GaNSs \) was between \(-58.36 \) to \(-61.06 \) and \(-76.83 \) to \(-76.30 \) kcal mol\(^{-1}\), respectively. The negative value of the AE indicates that adsorption of \( SO_2 \) and \( NO_2 \) on Ti doped \( GaNSs \) is an exothermic process. The adsorption energy of \( SO_2 \) and \( NO_2 \) on \( Ti\textsubscript{Ga}-GaNSs \) is greater than that of \( Ti\textsubscript{Ga}-GaNSs \). The obtained results indicate that the adsorption capability of \( Ti\textsubscript{Ga}-GaNSs \) is greater than that of \( Ti\textsubscript{Ga}-GaNSs \). Our results show that for the \( SO_2-Ti\textsubscript{Ga}-GaNSs \) and \( NO_2-Ti\textsubscript{Ga}-GaNSs \) complexes, the averages of the three binding distances (Ti–N) are 1.901 Å and 1.899 Å, respectively. For the \( SO_2-Ti\textsubscript{N}-GaNSs \) and \( NO_2-Ti\textsubscript{N}-GaNSs \) complexes, the averages of the three binding distances (Ti–Ga) are 2.983 Å and 2.949 Å, respectively. The calculated averages of the bond lengths of the S–O and N–O bonds in \( SO_2-Ti\textsubscript{Ga}-GaNSs \), \( SO_2-Ti\textsubscript{N}-GaNSs \), \( NO_2-Ti\textsubscript{Ga}-GaNSs \) and \( NO_2-Ti\textsubscript{N}-GaNSs \) have increased from 1.482 and 1.201 Å to 1.576, 1.606, 1.274 and 1.288 Å, respectively. These results show that the change in the \( SO_2 \) and \( NO_2 \) bond lengths upon adsorption on the \( Ti\textsubscript{N}-GaNSs \) is greater than those of \( Ti\textsubscript{Ga}-GaNSs \).

3.3. Adsorption of \( SO_2 \) and \( NO_2 \) gas molecules over Ti-doped \( GaNSs \)

Now, we investigate the adsorption of \( SO_2 \) and \( NO_2 \) gas molecules on the Ti-doped \( GaNSs \) as displayed in Fig. 3. Our results show that for the \( SO_2-Ti\textsubscript{Ga}-GaNSs \) and \( NO_2-Ti\textsubscript{Ga}-GaNSs \) complexes, the averages of the three binding distances (Ti–N) are 1.901 Å and 1.899 Å, respectively. For the \( SO_2-Ti\textsubscript{N}-GaNSs \) and \( NO_2-Ti\textsubscript{N}-GaNSs \) complexes, the averages of the three binding distances (Ti–Ga) are 2.983 Å and 2.949 Å, respectively. The calculated averages of the bond lengths of the S–O and N–O bonds in \( SO_2-Ti\textsubscript{Ga}-GaNSs \), \( SO_2-Ti\textsubscript{N}-GaNSs \), \( NO_2-Ti\textsubscript{Ga}-GaNSs \) and \( NO_2-Ti\textsubscript{N}-GaNSs \) have increased from 1.482 and 1.201 Å to 1.576, 1.606, 1.274 and 1.288 Å, respectively. These results show that the change in the \( SO_2 \) and \( NO_2 \) bond lengths upon adsorption on the \( Ti\textsubscript{N}-GaNSs \) is greater than those of \( Ti\textsubscript{Ga}-GaNSs \).

The Hirshfeld population analysis presents that the charges on Ti-doped \( GaNSs \) are transferred from the metal atom to the neighbor atoms and stabilization of single-metal doped \( GaNSs \). Besides, the positive charge of the M atom in \( M-GaNSs \) leads to the strong bonding between the M atom and its neighbor atoms and stabilization of single-metal doped \( GaNSs \). Besides, the positive charge of the M atom in \( M-GaNSs \) is more than \( M\textsubscript{Ga}GaNSs \), in good agreement with their binding energy (BE) and the average value of the M–NS bond length. Thus, because of greater transfer of charge between the nanosheet and M atoms in the \( M-GaNSs \) with respect to the corresponding \( M\textsubscript{Ga}GaNSs \), the \( M\textsubscript{Ga}GaNSs \) are predicted to be more stable than \( M\textsubscript{Ga}GaNSs \).
acceptors. There is a correlation between charge transfer values and adsorption energy in the process of adsorption of SO$_2$ and NO$_2$ on the GaNNSs. Comparison of charge transfer values between M-doped GaNNSs and SO$_2$ and NO$_2$ molecules demonstrate that the value for adsorption of NO$_2$ is greater than that of the corresponding SO$_2$ one, with the exception of that obtained for CrGa-GaNNS. This indicates that other parameters than charge transfer are responsible for the stability of the complexes.

The electron populations of orbitals given in Table 2 show that population of d-orbitals as well as total population of the M metals decrease upon the interaction of gases with Ti$_{Ga,N}$-GaNNSs. Besides, total electron population of orbitals in gases increases after adsorption of gases on the surface. This finding reveals that gases will take the electrons from Ti$_{Ga,N}$-GaNNSs. After adsorption of gases, total electron populations of orbitals of NO$_2$ (0.522e for NO$_2$-Ti$_{Ga,N}$-GaNNS and 0.500e for NO$_2$-Ti$_N$-GaNNS).

Table 4 Adsorption energy (AE), the shortest equilibrium distance between molecules and nanosheet (D) and Hirshfeld charge transfer (CT) for the most stable configurations of SO$_2$ and NO$_2$ on metal doped GaNNSs.

| Configurations       | AE (kcal mol$^{-1}$) | D (Å) | CT$^a$ (e) |
|----------------------|----------------------|-------|------------|
| NO$_2$               | 0.00                 |       |            |
| NO$_2$-Ti$_{Ga,N}$-GaNNS | −76.83               | 2.025 | 0.21       |
| NO$_2$-Ti$_N$-GaNNS  | −70.68               | 2.048 | 0.25       |
| NO$_2$-Cr$_{Ga,N}$-GaNNS | −54.79               | 1.912 | 0.22       |
| NO$_2$-Cr$_N$-GaNNS  | −60.81               | 1.952 | 0.31       |
| SO$_2$               | 0.00                 |       |            |
| SO$_2$-Ti$_{Ga,N}$-GaNNS | −61.06               | 2.000 | 0.16       |
| SO$_2$-Ti$_N$-GaNNS  | −58.36               | 1.896 | 0.21       |
| SO$_2$-Cr$_{Ga,N}$-GaNNS | −49.46               | 1.834 | 0.27       |
| SO$_2$-Cr$_N$-GaNNS  | −53.28               | 2.124 | 0.26       |

$^a$ Absolute value of the sum of atomic charges in complexed gases.
GaNNSs) are greater than those of SO2 (0.343 e for SO2–TiGa-GaNNs and 0.421 e for SO2–TiN-GaNNS), in good agreement with the greater AEs found for NO2–TiGa,GaNNs and NO2–TiN-GaNNS, respectively, in good agreement with the greater AE found for SO2–TiGa,GaNNs.

3.4. Adsorption of SO2 and NO2 gas molecules over Cr-doped GaNNNs

For the SO2–CrGa-GaNNS and NO2–CrGa,GaNNs complexes, the averages of three binding distances (Ti–N) are 1.834 Å and 1.912 Å, respectively. The calculated averages of bond lengths of S–O and N–O bonds in SO2–CrGa,GaNNs, SO2–CrN,GaNNs, NO2–CrGa,GaNNs and NO2–CrN,GaNNs have increased from 1.482 Å to 1.527, 1.574, 1.277 and 1.307 Å, respectively. For the SO2–CrN,GaNNs and NO2–CrN,GaNNs complexes, the averages of the three binding distances (Ti–Ga) are 2.124 Å and 1.952 Å, respectively. These results show that the change in the SO2 and NO2 bond lengths upon adsorption on the CrN,GaNNs is greater than that for CrGa,GaNNs. The optimized structures of the NO2 and SO2 adsorbed on Cr-doped GaNNNs are illustrated in Fig. 4. The modified surface of the Cr-doped GaNNNs facilitates the doped region to interact with approaching SO2 and NO2 molecules because of the higher chemical reactivity of the doped M atom. The results show that the SO2–...Cr distance for the SO2–

| Configurations     | $E_{\text{HOMO}}$ (eV) | $E_{\text{LUMO}}$ (eV) | $E_g$ (eV) | $\Delta E_g$ (eV) |
|--------------------|-------------------------|-------------------------|------------|-------------------|
| GaNNs              | –5.75                   | –3.23                   | 2.52       | –                  |
| TiGa,GaNNs         | –3.76                   | –3.28                   | 0.47       | 2.05              |
| TiN,GaNNs          | –4.50                   | –3.60                   | 0.90       | 1.62              |
| CrGa,GaNNs         | –4.28                   | –3.64                   | 0.64       | 1.88              |
| CrN,GaNNs          | –4.26                   | –3.78                   | 0.47       | 2.05              |
| NO2–GaNNs          | –5.83                   | –5.53                   | 0.29       | 2.23              |
| NO2–TiGa,GaNNs     | –5.90                   | –5.62                   | 2.28       | 1.81              |
| NO2–TiN,GaNNs      | –4.96                   | –4.01                   | 0.95       | 0.05              |
| NO2–CrGa,GaNNs     | –4.52                   | –3.87                   | 0.65       | 0.01              |
| NO2–CrN,GaNNs      | –5.08                   | –4.18                   | 0.91       | 0.44              |
| SO2–GaNNs          | –5.90                   | –3.37                   | 2.11       | 0.41              |
| SO2–TiGa,GaNNs     | –4.69                   | –3.29                   | 1.39       | 0.92              |
| SO2–TiN,GaNNs      | –4.39                   | –3.47                   | 1.11       | 0.21              |
| SO2–CrGa,GaNNs     | –3.45                   | –2.91                   | 0.53       | 0.11              |
| SO2–CrN,GaNNs      | –3.82                   | –3.53                   | 0.28       | 0.19              |

Fig. 5 The electron density schema (top and side views) of SO2 or NO2 adsorbed on doped GaNNNs with isovalue = 0.2e Å⁻³.
Cr$_{cr}$-GaNNs complex is larger than that for the SO$_2$–Cr$_{ga}$-GaNNs
one. Also, the NO$_2$–Cr distance for the NO$_2$–Cr$_{cr}$-GaNNs
complex is larger than that for NO$_2$–Cr$_{ga}$-GaNNs, indicating
that interaction in these complexes is stronger than for other ones.

The adsorption energies for SO$_2$ adsorbed on Cr$_{cr}$-GaNNs
and Cr$_{cr}$-GaNNs are $-40.46$ and $-53.28$ kcal mol$^{-1}$ and those
for NO$_2$ are $-54.79$ and $-60.81$ kcal mol$^{-1}$, respectively. The
negative value of the AE indicates that adsorption of SO$_2$ and
NO$_2$ on Cr doped GaNNs is an endothermic process. It is found
that the ability of Cr$_{cr}$-GaNNs towards adsorption of SO$_2$ and
NO$_2$ molecules is in the sequence NO$_2$–Cr$_{cr}$-GaNNs > SO$_2$–Cr$_{cr}$-
GaNNs and that of Cr$_{ga}$-GaNNs is in the order NO$_2$–Cr$_{ga}$-GaNNs
> SO$_2$–Cr$_{ga}$-GaNNs. In addition, it is found that SO$_2$ and NO$_2$
adsorption energies on Cr$_{cr}$GaNNs are greater than on Cr$_{ga}$-GaNNs.
The obtained results indicate that the adsorption capability of Cr$_{cr}$-GaNNs
is greater than Cr$_{ga}$-GaNNs. Our results show that SO$_2$ and NO$_2$
molecules are chemically adsorbed on all M-doped GaNNs.

The Hirshfeld population analysis shows that the charges are
transferred from the Cr$_{Ga-N}$-GaNN complexes to the SO$_2$
and NO$_2$ molecules. As can be seen in Table 4, the CT
values are $0.22e$, $0.31e$, $0.27e$ and $0.26e$ in NO$_2$–Cr$_{cr}$-GaNNs,
NO$_2$–Cr$_{ga}$-GaNNs, SO$_2$–Cr$_{cr}$-GaNNs and SO$_2$–Cr$_{ga}$-GaNNs,
respectively. This finding reveals that the charge transferred from
the nanosheet to the gas in NO$_2$–Cr$_{cr}$-GaNNs is greater than in other
complexes, in good agreement with the greater AE obtained for
these complexes. It should be noted that other parameters than
charge transfer can affect the adsorption of gases.

Analysis of the electron population of orbitals involved in the
interaction between gases and nanosheets given in Table 2
reveals that the total electron population of Cr decreases by
$-0.040e$, $-0.097e$, $-0.071e$ and $-0.172e$ in NO$_2$–Cr$_{cr}$-GaNNs,
NO$_2$–Cr$_{ga}$-GaNNs, SO$_2$–Cr$_{cr}$-GaNNs, SO$_2$–Cr$_{ga}$-GaNNs,
respectively, in good agreement with the greater AE found for
NO$_2$(SO$_2$)–Cr$_{cr}$GaNNs compared with NO$_2$(SO$_2$)–Cr$_{ga}$GaNNs.
In addition, the results show that the population of d-orbitals of
Cr decreases and those of the NO$_2$ and SO$_2$ gases increase upon
interaction with Cr$_{Ga-N}$-GaNNs. This finding demonstrates that
gases will get electrons from Cr$_{Ga-N}$-GaNNs, in good agreement
with the computed Hirshfeld charge transfer from the surface to
adsorbed gases.

3.5. HOMO and LUMO based electronic properties

There is an obvious difference between the electronic properties
of doped and undoped GaNNs. As can be seen in Table 5,
compared to pristine GaNNs, the energy of the highest occupied
molecule orbital (HOMO) increases and that of the lowest un-
occupied molecular orbital (LUMO) decreases in doped
GaNNs so that the amount of increase in HOMO is greater than
decrease in LUMO. After adsorption of NO$_2$, the energies of the
HOMO and LUMO decrease, but the LUMO energy shows
a further decrease. In the case of SO$_2$, adsorption of gas on the
Ti-doped GaNNs decreases both the HOMO and LUMO, but its
adsorption on the Cr-doped GaNNs increases them. These
changes in HOMO and LUMO energy levels lead to a change in
the HOMO–LUMO gap and, in turn, in the electronic properties
of GaNNs.

The results indicate that the band gap energies in both M$_{Ga,N}$
doped GaNNs are smaller than the pure GaNNs, making it
more conductive. The results given in Table 5 demonstrate that
the band gap value of pristine GaNNs is $2.52$ eV that changes to
$2.11$ eV in SO$_2$–GaNNs and $0.29$ eV in NO$_2$–GaNNs. Because
of the greater decrease in the LUMO level in NO$_2$–GaNNs with
respect to that of SO$_2$–GaNNs, the change in the band gap for
SO$_2$–GaNNs is lesser than for NO$_2$–GaNNs. Therefore, it is
predicted that GaNNs is more sensitive to NO$_2$ gas than SO$_2$ gas.
So, the large changes in band gap value for GaNNs ($2.52$ to $0.29$
eV) with NO$_2$ gas molecule adsorption can lead to a significant
change in electrical conductivity.

The electronic properties of doped GaNNs are affected by
the adsorption of SO$_2$ and NO$_2$ molecules. Upon adsorption of
SO$_2$ and NO$_2$ molecules on the Ti$_{Ga-N}$-GaNN complexes the
energy gap decreases in comparison with the pristine GaNNs.
The energy gap values are in the sequences SO$_2$–Ti$_N$-GaNNs
($1.11$ eV) > NO$_2$–Ti$_N$-GaNNs ($0.95$ eV) and NO$_2$–Ti$_{Ga}$-GaNNs
($2.28$ eV) > SO$_2$–Ti$_{Ga}$-GaNNs ($1.39$ eV). Reduction of the band gap
for SO$_2$–Ti$_N$-GaNNs is more than for NO$_2$–Ti$_N$-GaNNs and that for
NO$_2$–Ti$_{Ga}$-GaNNs is more than for SO$_2$–Ti$_{Ga}$-GaNNs. Therefore,
it can be concluded that the sensitivity of Ti$_N$-GaNN to SO$_2$ gas
adsorption on Ti$_N$-GaNNs is larger than that for Ti$_{Ga}$-GaNNs.
is greater than to NO₂ gas. Besides, for Ti₉Ga-GaNNS, it is predicted that the sensitivity to NO₂ gas is more than to SO₂ gas. It is a well-known issue that reduction of the energy gap enhances the electrical conductivity. Thus, the electrical conductivities are predicted to be in the order SO₂–Ti₉-GaNNS > NO₂–Ti₉-GaNNS and NO₂–Ti₉Ga-GaNNS > SO₂–Ti₉Ga-GaNNS.

Also, after adsorption of SO₂ and NO₂ molecules on the Cr₉Ga₉N-GaNNS complexes the band gap decreases in comparison with the pristine GaNNS. The band gap values are in sequence NO₂–Cr₉Ga₉N-GaNNS (0.91 eV) > SO₂–Cr₉Ga₉N-GaNNS (0.28 eV) and NO₂–Cr₉Ga₉N-GaNNS (0.65 eV) > SO₂–Cr₉Ga₉N-GaNNS (0.53 eV). The reduction in band gap for SO₂–Cr₉Ga₉N-GaNNS is more than for NO₂–Cr₉Ga₉N-GaNNS and that for NO₂–Cr₉N-GaNNS is more than for SO₂–Cr₉N-GaNNS. In consequence, the conductivities of SO₂–Cr₉Ga₉N-GaNNS and NO₂–Cr₉N-GaNNS are greater than NO₂–Cr₉Ga₉N-GaNNS and SO₂–Cr₉N-GaNNS, respectively. Also, from the changes in band gap energy values, it is forecast that the sensitivity of Cr₉N-GaNNS to NO₂ gas is more than to SO₂ gas.

Fig. 7  The densities of states (DOSs) of SO₂ or NO₂ adsorbed on doped GaNNSs.
The top and side view plots of the electron density are illustrated in Fig. 5. An orbital overlap can be observed between the NO$_2$ (SO$_2$) gas molecules and the GaN sheets, revealing the occurrence of a strong chemisorption. It is clearly displayed that the electrons dominantly accumulate in the region between gases and GaN NSs. These results are in accordance with the obtained adsorption energies and binding distances. The orbital mixing and the charge transfer are expected to bring significant changes to the electronic structure of the GaN nanosheets which is beneficial for sensing applications. The isovalue for adsorption of gas molecules on GaN NSs is 0.2\(\text{e}\) \(\text{Å}^{-3}\).

To obtain a better understanding about the electronic properties of the complexes, densities of states (DOSs) of the nanostructures are calculated and visualized in Fig. 6 and 7. As can be observed, the GaNNS, NO$_2$–GaNNS, SO$_2$–GaNNS, NO$_2$–Ti$_{Ga}$-GaNNS, NO$_2$–In$_{Ga}$-GaNNS and NO$_2$–Cr$_{N}$-GaNNS nanostructures are nonmagnetic systems because the spin-up and spin-down in the DOS plots are the same as each other. From this figure, it can be found that new states appear in the band gap regions of NO$_2$–Cr$_{Ga}$-GaNNS, SO$_2$–Ti$_{Ga}$-GaNNS, SO$_2$–Ti$_{N}$-GaNNS, SO$_2$–Cr$_{Ga}$-GaNNS and SO$_2$–Cr$_{N}$-GaNNS. Since the spin-up and spin-down DOSs are different, NO$_2$–Cr$_{Ga}$-GaNNS, SO$_2$–Ti$_{Ga}$-GaNNS, SO$_2$–Ti$_{N}$-GaNNS, SO$_2$–Cr$_{Ga}$-GaNNS and SO$_2$–Cr$_{N}$-GaNNS have magnetic properties.

4. Conclusions

DFT calculations are performed to consider the adsorption of sulfur dioxide and nitrogen dioxide molecules on metal-doped gallium nitride nanosheets. The results present that adsorption of NO$_2$ on Mn$_{Ga}$-GaNNS and M$_{Ga}$-GaNNS is energetically more favorable than that of SO$_2$ on corresponding NSs. A brief comparison of AEs of SO$_2$ and NO$_2$ molecules on Ti and Cr doped GaNNSs indicates that the AEs of NO$_2$ and SO$_2$ on Ti$_{Ga}$,N-GaNNSs are greater than on Cr$_{Ga}$,N-GaNNSs. The electron populations of orbitals were calculated before and after interaction. There is a correlation between the change in electron population of orbitals of adsorbate and adsorbed and the AE obtained for complexes. The electron population analysis shows that charge is transferred from M$_{Ga}$,N-GaNNSs to the adsorbed gases. After the adsorption of SO$_2$ and NO$_2$ molecules, the electronic properties of the pure and doped GaNNSs indicate the considerable changes in the conductivity of the nanosheets. Furthermore, the sensitivity of Ti$_{Ga}$-GaNNS is predicted to be more than for other NSs toward SO$_2$ gas. It is estimated that the sensitivity of Ti$_{Ga}$-GaNNS to NO$_2$ gas is more than to SO$_2$ gas. Therefore, these results show that GaNNS-based materials can be used as noxious gas sensors.

Conflicts of interest

The all authors declare that they have no conflict of interest.

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