Adsorption of NO₂ and H₂S on ZnGa₂O₄(111) Thin Films: A First-Principles Density Functional Theory Study

Jen-Chuan Tung ¹, Yi-Hung Chiang ², Ding-Yuan Wang ² and Po-Liang Liu ²,*

¹ Center for General Education, China Medical University, Taichung 404, Taiwan; jenchuan.tung@gmail.com
² Graduate Institute of Precision Engineering, National Chung Hsing University, Taichung 402, Taiwan; ylp51112@gmail.com (Y.-H.C.); ss971331@gmail.com (D.-Y.W.)
* Correspondence: pliu@dragon.nchu.edu.tw; Tel.: +886-921-820915

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Featured Application: This work offers a detailed description of gas-sensing performance of ZnGa₂O₄-based gas sensors.

Abstract: We performed first-principles total-energy density functional calculations to study the reactions of NO₂ and H₂S molecules on Ga–Zn–O-terminated ZnGa₂O₄(111) surfaces. The adsorption reaction and work functions of eight NO₂ and H₂S adsorption models were examined. The bonding of the nitrogen atom from a single NO₂ molecule to the Ga atom of the Ga–Zn–O-terminated ZnGa₂O₄(111) surfaces exhibited a maximum work function change of +0.97 eV. The bond joining the sulfur atom from a single H₂S molecule and the Ga atom of Ga–Zn–O-terminated ZnGa₂O₄(111) surfaces exhibited a maximum work function change of −1.66 eV. Both results concur with previously reported experimental observations for ZnGa₂O₄-based gas sensors.

Keywords: ZnGa₂O₄; NO₂; H₂S; work function; first-principles calculations

1. Introduction

Household and industrial gas sensors are of great significance in artificial intelligence systems [1]. However, several key problems and challenges persist in the development of sensing components. The sensor has an operating temperature that is too high for it to be used as a wearable device; moreover, wearable devices are subject to moisture, which weakens their sensing efficiency. Other problems are the difficulty of distinguishing the composition and concentration of the mixing gases and the inaccuracy of sensing results. Metal oxide compounds, such as tin oxide (SnO₂), gallium oxide (Ga₂O₃), and titanium dioxide (TiO₂) semiconductor materials, have excellent potential for sensing applications and can detect harmful and toxic gases in the temperature range of 300–550 °C [2]. Kolmakov et al., reported that tin oxide nanowire sensors can sense the oxidizing gas of oxygen (O₂) and the reductive gas of carbon monoxide (CO) at temperatures between 200 and 280 °C [3]. Schwebel et al., reported that β-Ga₂O₃ films can be used to sense reductive gases such as CO, hydrogen (H₂), methane (CH₄), nitric oxide (NO), and ammonia (NH₃) [4]. Liu et al., reported that Ga₂O₃ nanowire gas sensors exhibit a reversible response to the oxidizing gases of O₂ and reductive gas of CO in a working temperature range of 100–500 °C [5]. The maximum response of the Ga₂O₃ nanowire gas sensors for CO gas is four times larger than that for hydrogen, ammonia, or hydrogen sulfide (H₂S) gas.

N-type semiconductors of ZnGa₂O₄ thin films have been developed, and ZnGa₂O₄ materials have been successfully used as gas sensors. Satyanarayana et al., reported that spinel ZnGa₂O₄ films can be used to sense liquid petroleum gas (LPG) at temperatures ranging from 200 to 400 °C. ZnGa₂O₄ sensors...
doped with palladium at approximately 320 °C have high selectivity to LPG, but poor sensitivity to CH₄ and CO [6]. Furthermore, Jiao et al., reported the use of ZnGa₂O₄ prepared by spraying coprecipitation for sensing LPG, CO, ethanol (C₂H₅OH), and methane [7]. A novel approach described in Chen et al., (2010) [8] is based on the use of ZnGa₂O₄/ZnO core–shell nanowires. Sensitivity to nitrogen dioxide (NO₂) gas can be considerably improved by using ZnGa₂O₄/ZnO core–shell nanowires rather than pure ZnO nanowires. Despite the introduction of new approaches to developing gas sensors, the fundamental interaction between gas molecules and metal oxide compounds remains unclear.

Density functional theory (DFT) calculations have been widely used in the fields of atomic and molecular adsorption on surfaces and the gas-sensing mechanism [9,10]. For example, water adsorption on the carbon nanotube field-effect transistor (CNTFET) explains the humidity-induced hysteresis, and it can be reasoned that water adsorption on the CNTFET leads to an increased chemical activity, the modification of the Schottky barrier, and the adsorption of some ionic substances in the vicinity of the carbon nanotube [9]. The gas-sensing mechanism of ZnO applied to H₂, NH₃, CO, and C₂H₅OH was established by conducting first-principles DFT calculations [10]. When the gas molecules, i.e., H₂, NH₃, CO, and C₂H₅OH molecules, become incident upon the ZnO(10-10) surface, the adsorption-induced reconstruction of the ZnO surface and charge transfer from the gas molecules to the ZnO surface control the sensing process evaluated by the change of electronic conductance of ZnO. Vorobyeva et al., reported that the resistance response of ZnO at operating temperature 450 °C increased (decreased) in the presence of NO₂ (H₂S) [11]. Moreover, the sensor responses of ZnO and ZnO with gallium contents of 0.5% and 4.0 at% show that an increase of gallium caused a monotonous decrease of the sensor response to H₂S due to the enhanced electron-donor ability of surface oxygen anions, the H–S bond-breaking in the H₂S molecule, as well as the decrease of the H₂S adsorption. Recently, we demonstrated epitaxial growth of ZnGa₂O₄ thin film grown on the sapphire substrate using a metalorganic chemical vapor deposition (MOCVD) technique that yields a high-selectivity gas sensor [12]. The ZnGa₂O₄ gas sensor has superior selectivity to NO at the operating temperature of 300 °C. Reactions of NO molecules on Ga–Zn–O-terminated ZnGa₂O₄(111) surfaces were modeled and carried out using a first-principles density functional theory method. The NO molecules combine with the gallium atoms on the ZnGa₂O₄(111) surface to produce N–Ga bonds, leading to the work function changes. The sensor response can be gained from the changes in the work functions, indicating that the N–Ga bonding exhibits a very sensitive adsorption response. In this study, we developed adequate models for accurately predicting toxic NO₂ oxidizing gases and H₂S reducing gases adsorbed on the ZnGa₂O₄(111) surface, which offer a detailed description of gas-sensing performance of the use of ZnGa₂O₄-based thin-film sensors, which may be probed experimentally using phenomenological techniques of sensor characterization such as chemical components, sensing layers, and surface modification by metal doping.

2. Computational Details

A series of ab initio calculations were performed to evaluate the adsorption reactions and work functions of NO₂ and H₂S on ZnGa₂O₄(111) surfaces. The ab initio theoretical results were implemented in the Vienna ab initio simulation package [13,14], and the exchange correlation function was predicted using the generalized gradient approximation (GGA) with the Perdew–Wang (PW91) correction [15,16]. The crystal structure of ZnGa₂O₄ is displayed in Figure 1. The space group for ZnGa₂O₄ is Fd-3m, which contains 56 atoms, comprising 8 Zn, 16 Ga, and 32 O atoms. The cutoff energy was set as 400 eV. To simulate the change of the work function with and without an NO₂ or H₂S molecule, we developed a supercell of ZnGa₂O₄ along the (111) direction. This supercell contained 112 atoms, and the vacuum was set to 20 Å. The stoichiometry of all supercells was fixed at Zn₁₆Ga₃₂O₆₄. We used the preferred Ga–Zn–O-terminated surface of ZnGa₂O₄(111) with a surface energy of 0.10 eV/Å² [17]. A gamma-centered 3 × 3 × 1 Monkhorst–Pack grid was used. This supercell was fully relaxed until the force acting on each atom was less than 0.001 eV/Å.
To determine the most favorable adsorption site of NO$_2$ ($\text{H}_2\text{S}$) molecules on the ZnGa$_2$O$_4$(111) surface, we labeled the surface atoms as Ga$_{3c}$, Zn$_{3c}$, O$_{3c}$, and O$_{4c}$ in the top and side views of Figure 2.

We first calculated the work function using the formula [18]

$$\Phi_{\text{ZGO}} = E_{\text{VAC}} - E_F$$  \hspace{1cm} (1)
where $\Phi_{\text{ZGO}}$ is the work function for the clean ZnGa$_2$O$_4$(111) surface and $E_{\text{VAC}}$ and $E_F$ are the energy of the vacuum and the Fermi energy, respectively. Similarly, when the NO$_2$ (H$_2$S) molecule was adsorbed on the ZnGa$_2$O$_4$(111) surface, we also calculated the work function $\Phi_{\text{NO}_2}$ and $\Phi_{\text{H}_2\text{S}}$, which in turn determined the work function differences $\Delta \Phi$ (eV) between $\Phi_{\text{ZGO}}$ and $\Phi_{\text{NO}_2}$ ($\Phi_{\text{H}_2\text{S}}$). The binding energy $E_B$ (eV/μ. c.) is also an important factor determining gas-sensing performance and can be defined as

$$E_B = E_{\text{total}} - E_{\text{ZGO}} - E_{\text{NO}_2/\text{H}_2\text{S}}$$  \hspace{1cm} (2)$$

where $E_{\text{total}}$ is the total energy of the NO$_2$ (H$_2$S) molecule adsorbed on the ZnGa$_2$O$_4$(111) surface, and $E_{\text{ZGO}}$ and $E_{\text{NO}_2/\text{H}_2\text{S}}$ are the total energies of the slab of ZnGa$_2$O$_4$(111) surface and the free or isolated NO$_2$ (H$_2$S) molecule, respectively.

First, we constructed eight adsorption models, denoted N1, N2, N3, N4, O1, O2, O3, and O4. Here, N (O) represents a nitrogen (oxygen) atom in NO$_2$, and numbers “1”, “2”, “3”, and “4” respectively indicate the initial adsorbed Ga$_{3c}$, Zn$_{3c}$, O$_{3c}$, and O$_{4c}$ atom on the ZnGa$_2$O$_4$(111) surface. The initial distance of the NO$_2$ molecule to the ZnGa$_2$O$_4$(111) surface was set as the sum of the van der Waal radii of N (O) for the NO$_2$ molecule and Ga (Zn or O) for surface atoms. Similarly, for the H$_2$S molecule adsorbed on the ZnGa$_2$O$_4$(111) surface, we also developed eight adsorption models, denoted S1, S2, S3, S4, H1, H2, H3, and H4. Here, S (H) represents a sulfur (hydrogen) atom in H$_2$S. The initial distance of the H$_2$S molecule to the ZnGa$_2$O$_4$(111) surface was also set as the sum of the van der Waal radii of H (S) and Ga (Zn or O) for surface atoms. We performed structure optimization in each model until the force acting on each atom was less than 0.001 eV/Å, yielding optimized atomic structures.

The gas sensitivity could be determined from the ratio of the resistance in the presence of the investigated gas ($R_g$) to the resistance in the reference gas ($R_a$), which is usually air [19]. The relation of gas sensitivity to the work function difference $\Delta \Phi$ is represented by the following equation:

$$\Delta \Phi = \Delta X + kT \ln (R_g/R_a)$$  \hspace{1cm} (3)$$

where $\Delta X$ denotes the change in electron affinity and $kT$ denotes the product of the Boltzmann constant $k$ and the temperature $T$. The upward bending of the surface band due to the adsorption of oxidizing gas on ZnGa$_2$O$_4$(111) results in the depletion of free charge carriers on the surface, thus leading to the formation of a region with high ohmic resistance or a positive work function difference. However, the resistance of ZnGa$_2$O$_4$(111) gas sensors decreases under exposure to reducing gases because of the downward bending of the surface band, resulting in a negative work function difference.

3. Results and Discussion

The most favorable configurations for NO$_2$ on ZnGa$_2$O$_4$ (111) surfaces are shown in Figure 3. In Model N1, the nitrogen atom of the NO$_2$ molecule was adsorbed on the Ga$_{3c}$ atom of the ZnGa$_2$O$_4$(111) surface to yield a N–Ga bond with a bond length of 2.01 Å. In Model N2, the NO$_2$ molecule moved away from the originally adsorbed Zn$_{3c}$ atom to approach the neighboring Ga atom of the ZnGa$_2$O$_4$(111) surface to form an O–Ga bond with a bond length of 1.90 Å. In Model N3, the NO$_2$ molecule moved away from the originally adsorbed O$_{3c}$ atom toward the neighboring Ga and Zn atoms of the ZnGa$_2$O$_4$(111) surface to form N–Ga and O–Zn bonds with bond lengths of 2.05 Å and 2.30 Å, respectively. In Model N4, the nitrogen (oxygen) atom of the NO$_2$ molecule adsorbed on the Ga$_{3c}$ (Zn$_{3c}$) atom of the ZnGa$_2$O$_4$(111) surface to form an N–Ga (O–Zn) bond with a bond length of 2.06 Å (2.21 Å). In Model O1, the two O atoms of the NO$_2$ molecule adsorbed on the Ga$_{3c}$ atom of the ZnGa$_2$O$_4$(111) surface to yield two O–Ga bonds with bond lengths of 2.07 Å and 2.13 Å. Similarly, in Model O2 (O3), the NO$_2$ molecule moved away from the originally adsorbed Zn$_{3c}$ (O$_{3c}$) atom toward the neighboring Ga$_{3c}$ atom of the ZnGa$_2$O$_4$(111) surface to form two O–Ga bonds with bond lengths of 2.10 (2.13) Å and 2.11 (2.08) Å. In Model O4, an O atom of the NO$_2$ molecule was adsorbed on the Ga$_{3c}$ atom of the ZnGa$_2$O$_4$(111) surface to form an O–Ga bond with a bond length of 1.92 Å. The vacuum energy, Fermi energy, work functions of ZnGa$_2$O$_4$(111) with and without NO$_2$, and work function difference among
NO$_2$ adsorption models are presented in Table 1. The work function increased when the NO$_2$ molecule was adsorbed on the ZnGa$_2$O$_4$(111) surface. The increase in work function ranged from +0.29 eV to +0.97 eV, which concurs with previously reported experimental results of similar resistance responses of ZnO(Ga) samples to NO$_2$ [8,11]. The NO$_2$ molecule preferred bonding with the Ga$_{3c}$ or Zn$_{3c}$ atom. Model N1 had the maximum work function difference of +0.97 eV, exhibiting increased sensitivity for detecting NO$_2$ molecules.

![Model N1, Model N2, Model N3, Model N4, Model O1, Model O2, Model O3, Model O4](image_url)

**Figure 3.** Top and side views of the favorable configurations for NO$_2$ on the ZnGa$_2$O$_4$(111) surface. Atoms are represented by spheres: Zn (purple, large), Ga (brown, large), S (yellow, medium-sized), O (red, medium-sized), and H (white, small). Equilibrium bond lengths between molecular and surface atoms are given in Angstrom.

**Table 1.** Calculated vacuum energy $E_{\text{VAC}}$, Fermi energy $E_F$, work function of NO$_2$ $\Phi_{\text{NO}_2}$, work function of ZnGa$_2$O$_4$(111) $\Phi_{ZGO}$, and work function difference $\Delta\Phi$ ($\Delta\Phi = \Phi_{\text{NO}_2} - \Phi_{ZGO}$) among the eight NO$_2$ adsorption models. All energies are presented in eV.

| Models        | Adsorption Sites | $E_{\text{VAC}}$ | $E_F$  | $\Phi_{\text{NO}_2}$ | $\Phi_{ZGO}$ | $\Delta\Phi$ |
|---------------|------------------|------------------|-------|----------------------|--------------|--------------|
| ZnGa$_2$O$_4$(111) | -                | 0.66             | -3.38 | -                    | 4.04         | -            |
| N1            | Ga$_{3c}$        | 1.45             | -3.56 | 5.01                 | -            | +0.97        |
| N2            | Ga$_{3c}$        | 1.04             | -3.29 | 4.33                 | -            | +0.29        |
| N3            | Ga$_{3c}$, Zn$_{3c}$ | 1.12            | -3.31 | 4.43                 | -            | +0.39        |
| N4            | Ga$_{3c}$, Zn$_{3c}$ | 1.09            | -3.31 | 4.40                 | -            | +0.36        |
| O1            | Ga$_{3c}$        | 0.98             | -3.41 | 4.39                 | -            | +0.35        |
| O2            | Ga$_{3c}$        | 1.01             | -3.36 | 4.37                 | -            | +0.33        |
| O3            | Ga$_{3c}$        | 1.07             | -3.31 | 4.38                 | -            | +0.34        |
| O4            | Ga$_{3c}$        | 1.04             | -3.29 | 4.33                 | -            | +0.29        |
Figure 4 displays the lowest energy configurations for H$_2$S on ZnGa$_2$O$_4$(111) surfaces. In Models S1 and S2, the sulfur atom of the H$_2$S molecule adsorbed on the Ga$_{3c}$ and Zn$_{3c}$ atoms of the ZnGa$_2$O$_4$(111) surface to yield S–Ga and S–Zn bonds with bond lengths of 2.46 Å and 2.50 Å, respectively. In Model S3, the H$_2$S molecule adsorbed on the O$_{3c}$ atom of the ZnGa$_2$O$_4$(111) surface and dissociated to HS$^-$ and H$^+$ ions to form H–O and S–Ga bonds with bond lengths of 0.97 Å and 2.22 Å, respectively. In Model S4, the H$_2$S molecule moved away from the originally adsorbed O$_{4c}$ atom of the ZnGa$_2$O$_4$(111) surface to form an S–Ga bond with a bond length of 2.46 Å. In Models H1 and H2, the H$_2$S molecules adsorbed on Ga$_{3c}$ and Zn$_{3c}$ atoms of the ZnGa$_2$O$_4$(111) surface and dissociated to H$^+$ and HS$^-$ ions to form an H–O bond and an S–Ga bond with bond lengths of 0.97 Å and 2.22 Å, respectively. In Model H3, the hydrogen atom of the H$_2$S molecule was adsorbed on the O$_{3c}$ atom of the ZnGa$_2$O$_4$(111) surface to yield an H–O bond with a bond length of 1.25 Å. In Model H4, the H$_2$S molecule adsorbed on the O$_{4c}$ atom of the ZnGa$_2$O$_4$(111) surface. However, its adsorption was unstable and therefore not ideal, with atomic distances of 3.12 Å and 2.66 Å for H–Ga and H–Zn, respectively.

Figure 4. Top and side views of the most favorable configurations for H$_2$S on the ZnGa$_2$O$_4$(111) surface. Atoms are represented by spheres: Zn (purple, large), Ga (brown, large), S (yellow, medium-sized), O (red, medium-sized), and H (white, small). Equilibrium bond lengths between molecular and surface atoms are given in Angstrom.

The vacuum energy, Fermi energy, work functions of ZnGa$_2$O$_4$(111) with and without H$_2$S, and work function difference among H$_2$S adsorption models are listed in Table 2. The work function difference among Models S1, S2, and S4 decreased when the H$_2$S molecules adsorbed on the Ga$_{3c}$ and Zn$_{3c}$ atoms of the ZnGa$_2$O$_4$(111) surface. The decrease in work function ranged from $-0.31$ to $-1.66$ eV, which concurs with the experimental results of other studies showing similar resistance responses of ZnO(Ga) samples to H$_2$S [11]. Similarly, the H$_2$S molecule preferred bonding with the Ga$_{3c}$ or Zn$_{3c}$ atom. Model S1 had the maximum work function difference of $-1.66$ eV, showing increased sensitivity for detecting H$_2$S molecules. Models S3, H1, H2, H3, and H4 had positive work function differences,
possibly because of the heterolytic break of the H–S bond in the H₂S, resulting in the tendency of forming H–O bonds on the surface of ZnGa₂O₄. The H–S bond-breaking leading to the decrease of the H₂S adsorption might explain the observed change in the decreased sensitivity for detecting H₂S molecules, in agreement with the experimental observation [11].

Table 2. Calculated vacuum energy $E_{\text{VAC}}$, Fermi energy $E_F$, work function of H₂S $\Phi_{\text{H₂S}}$, work function of ZnGa₂O₄(111) $\Phi_{\text{ZGO}}$, and work function difference $\Delta \Phi (\Delta \Phi = \Phi_{\text{H₂S}} - \Phi_{\text{ZGO}})$ among the eight H₂S adsorption models. All energies are presented in eV.

| Models Adsorption Sites | $E_{\text{VAC}}$ | $E_F$ | $\Phi_{\text{H₂S}}$ | $\Phi_{\text{ZGO}}$ | $\Delta \Phi$ |
|------------------------|------------------|-------|---------------------|---------------------|--------------|
| ZnGa₂O₄(111) Ga₃c     | -                | 0.66  | -3.38               | -                   | 4.04         |
| S1                     | Ga₃c             | -0.37 | -2.75               | 2.38                | -0.16        |
| S2                     | Zn₃c             | 0.54  | -3.19               | 3.73                | -0.31        |
| S3                     | Ga₃c, O₁c        | 0.91  | -3.32               | 4.23                | +0.19        |
| S4                     | Ga₃c             | -0.51 | -2.91               | 2.40                | -1.64        |
| H1                     | Ga₃c, O₁c        | 0.90  | -3.32               | 4.22                | +0.18        |
| H2                     | Ga₃c, O₁c        | 0.94  | -3.32               | 4.26                | +0.22        |
| H3                     | O₁c              | 0.79  | -3.37               | 4.16                | -0.12        |
| H4                     | -                | 0.85  | -3.47               | 4.32                | +0.28        |

4. Conclusions

The adsorption reactions and work functions of NO₂ and H₂S on ZnGa₂O₄(111) surfaces were studied using first-principles DFT–GGA calculations. Our results showed that the bonding of the nitrogen (sulfur) atom from a single NO₂ (H₂S) molecule to the Ga atom of Ga–Zn–O-terminated ZnGa₂O₄(111) surfaces exhibited the highest work function change of +0.97 eV (−1.66 eV). Experiments on the resistance responses of ZnO(Ga) samples to NO₂ (H₂S) molecules revealed that sensitivity responses to NO₂ (H₂S) molecules of ZnGa₂O₄-based thin-film sensors exhibit the same trend as that of positive (negative) work function differences [11]. In our favorable configuration, both NO₂ and H₂S molecules preferred bonding with the Ga₃c atom of Ga–Zn–O-terminated ZnGa₂O₄(111) surfaces. The results demonstrate the sensitivity responses to NO₂ and H₂S molecules of ZnGa₂O₄-based thin-film sensors, which concur with experimental observations of ZnGa₂O₄-based gas sensors. The thin-film pretreatment technology, such as the thin-film coatings resulting in a Ga-terminated surface, could enhance the sensitivity responses of future gas-sensing devices.

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