

Article

Ab Initio Studies of Work Function Changes of CO Adsorption on Clean and Pd-Doped ZnGa₂O₄(111) Surfaces for Gas Sensors

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Featured Application: This work provides a detailed analysis on the gas-sensing performance of Pd-doped ZnGa₂O₄-based sensors for detecting CO gas.



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Abstract: We performed first-principles calculations to study the adsorption of the CO molecules on both clean and Pd-doped ZnGa₂O₄(111) surfaces. The adsorption reaction and work function of the CO adsorption models were examined. The CO molecules on the clean and Pd-doped ZnGa₂O₄(111) surfaces exhibit maximum work function changes of −0.55 eV and −0.79 eV, respectively. The work function change of Pd-doped ZnGa₂O₄(111) for detecting CO is 1.43 times higher than that of the clean ZnGa₂O₄(111). In addition, the adsorption energy is also significantly reduced from −1.88 eV to −3.36 eV without and with Pd atoms, respectively. The results demonstrate ZnGa₂O₄-based gas sensors doped by palladium can improve the sensitivity of detecting CO molecules.

Keywords: first-principles calculation; ZnGa₂O₄ surface; work function; palladium

1. Introduction

Environmental sensing is an important input information required by current artificial intelligence. Connecting artificial intelligence through new-generation sensing elements will be applied to human living environments, such as harmful pollution sources in the air, toxic substances generated during processing and production, or biogas in an oxygen-deficient environment. How to improve the sensitivity and the detection gas range is an important research topic of the new generation of sensing elements. The rapid increase in the market demand for artificial intelligence will drive the development of new-generation sensing components. At present, there are still many key technologies for environmental sensing to be overcome. For example, the gas sensors on the market are bulky and need to be installed in a fixed position or hand-held for detection. Recently, we have demonstrated that ZnGa₂O₄(111) films are grown directly on Al₂O₃(0001) using a metalorganic chemical vapor deposition (MOCVD) technique and applied in CO, CO₂, SO₂, NO, and NO₂ gas detection [1]. In the presence of oxidizing gas on the *n*-type ZnGa₂O₄ semiconductor, electrons flow from the *n*-type semiconductor to the oxidizing gas until the Fermi level equilibrium is reached, which causes surface energy band bending [2–5]. The magnitude of

surface band bending is the difference between the work function and electron affinity of target gases on $\text{ZnGa}_2\text{O}_4(111)$ surfaces. The surface energy band bending makes it difficult for electrons inside the semiconductor to migrate to the surface, thereby increasing the surface resistance of the semiconductor. In contrast, when the reducing gas contacts the n -type ZnGa_2O_4 semiconductor, electrons flow from the reducing gas to the n -type semiconductor until the Fermi level is balanced, which results in ohmic contact formation [2–5]. Ohmic contact means that the current can flow in both directions at the junction between the reducing gas and the semiconductor, and the ohmic contact make the electrons inside the semiconductor easily migrate to the surface, thereby reducing the surface resistance of the semiconductor.

Recently, we have demonstrated that an NO_2 -oxidizing and H_2S -reducing molecule adsorbed on the Ga–Zn–O-terminated $\text{ZnGa}_2\text{O}_4(111)$ surface exhibit the highest work function change of +0.97 eV and –1.66 eV, respectively [2]. Pd-decorated $\text{ZnGa}_2\text{O}_4(111)$ sensors also exhibit high selectivity to NO_2 gas detectors, which have the maximum work function change of +1.37 eV and +2.37 eV for one and two NO_2 molecules to a Pd atom, respectively [5]. In contrast, the work function change of one H_2S molecule on the Pd-decorated $\text{ZnGa}_2\text{O}_4(111)$ surface is reduced to –0.90 eV, resulting in the decrease in sensitivity to a palladium adsorbed on the $\text{ZnGa}_2\text{O}_4(111)$ surface [5]. In this regard, the work function changes of two H_2S molecules on the Pd-decorated $\text{ZnGa}_2\text{O}_4(111)$ surface changes significantly to –1.82 eV or shows a trend of increasing sensitivity with increasing gas molecule concentration [5]. The gas sensing sensitivity is not only dependent on the work function change, but also related to the adsorption energy of gas molecules. The adsorption energy of gas molecules with exothermic reaction can spontaneously react to cause gas molecule adsorption, so that the gas sensing sensitivity can be estimated by the change of the work function [5]. However, the adsorption energy of an NO_2 (H_2S) molecule adsorbed to the $\text{ZnGa}_2\text{O}_4(111)$ surface is 0.64 eV (2.32 eV), showing that the positive adsorption energy or the corresponding endothermic process can be supported by an increase in temperature [5]. High positive adsorption energy means that more external energy is required, suggesting that the film is not easy to attract gas molecules and the sensitivity will be limited even under large work function changes.

In this study, we pursued the gas-sensing mechanism of the adsorption of CO-reducing molecules on a clean $\text{ZnGa}_2\text{O}_4(111)$ and Pd-decorated $\text{ZnGa}_2\text{O}_4(111)$ surfaces. Human inhalation of carbon monoxide will combine with hemoglobin in the human body and diminish the hemoglobin's oxygen-carrying capacity, resulting in tissue hypoxia [6]. The lack of oxygen in the human body will cause dizziness, headache, nausea, weakness, and other symptoms, and in severe cases, coma, convulsions, and even death. The development of CO sensors has been an important and popular research topic for a long time [1,2,5,7–11]. For example, Yu et al. reported the sensitivity of CO gas detection of the CuO- and ZnO-doped SnO_2 gas sensor [7]. The maximum sensitivity of SnO_2 to 200 ppm CO is 7 at 350 °C, while the addition of 1 mol% CuO and 3 mol% ZnO increases the sensitivity of SnO_2 sensor to 8 at 200 °C. Gong et al. prepared Cu-doped ZnO (CZO) thin films on glass substrates by cosputtering using ZnO and Cu targets [8]. The CZO films with the columnar structures consisted of small crystals with an average grain size of about 5 nm. The CO sensing properties of the CZO films exhibit the highest sensitivity to 40 ppm CO at 350 °C, while the resistance values of the CZO films are also observed when the sensor is exposed to 6 ppm CO at 150 °C. Paliwal et al. reported that ZnO sensing films deposited on gold-coated prisms exhibit high sensitivity with very fast response to CO gas in a wide concentration range (0.5–100 ppm) at room temperature [9]. Belmonte et al. proposed a micromachined twin sensor, which consists of two sensing layers, a sensing layer made of $\text{Cr}_x\text{Ti}_y\text{O}_2$, and a SnO_2 metal oxide gas sensing layer [10]. When the reducing gas CO interacts with the sensing surface, the n -type SnO_2 gas sensor materials can obtain more electrons, thereby reducing the resistance value of the SnO_2 material. Chang et al. studied a palladium-doped ZnO gas sensor to detect CO gas [11]. The sensitivity of the palladium-doped ZnO (Pd/ZnO) was 4.5 times higher than that of ZnO when the CO concentration

was 100 ppm. The Pd/ZnO injected with CO concentrations of 10–600 ppm shows a decrease in the resistance responses, whereas ZnO shows no significant change under the CO concentrations of 10–600 ppm. The response time of Pd/ZnO at a CO concentration of 100 ppm is 200 s, compared with 750 s for ZnO, which indicates that the change of the response time of Pd/ZnO is three times shorter than that of ZnO. The experimental results show that doping palladium helps to improve the sensitivity and response time of the ZnO sensor.

Gallium(III) oxide is another material of interest due to its large bandgap and physical and chemical stability. Tin-doped Ga₂O₃ improves material conductivity, which makes the higher Lewis acidity of Sn⁴⁺ cations than Ga³⁺ ones, which leads to a significant sharp increase in sensor signal for detecting CO and NH₃ at high temperature of 500 °C [12]. On the other hand, carbon dioxide adsorption on the nonpolar (10 $\bar{1}$ 0) surface of ZnO shows the tridentate binding mode to be the most energetically favorable, which the internal C=O bonds of CO₂ lengthened upon adsorption from the initial value from 1.16 Å to 1.26–1.24 Å [13]. If defective surface with one oxygen vacancy on the nonpolar (10 $\bar{1}$ 0) surface of ZnO exists, the adsorption of carbon dioxide on the surface causes the oxygen atom in CO₂ to be trapped, acting as a CO molecule remaining on the surface. For deep ultraviolet applications integrated on *c*-plane (002) sapphire substrates, the ZnGa₂O₄ thin films were prepared using the diethylzinc (DEZn), triethylgallium (TEGa), and oxygen (99.999%), and were transformed from β -Ga₂O₃ to ZnGa₂O₄ with increasing DEZn flow rate [14]. This is because the sufficient tensile strain in Zn-doped β -Ga₂O₃ provides a driving force for ZnGa₂O₄ formation, obtaining the carrier concentrations up to $6.72 \times 10^{16} \text{ cm}^{-3}$ and the resistivity down to 67.9 $\Omega\cdot\text{cm}$. For applications of green storage and long persistent phosphors, ZnGa₂O₄ spinel ceramics doped with Mn²⁺ ions were prepared by a solid-state reaction at 1200 °C in air and demonstrated a relatively long and strong green afterglow due to the holes released from shallow traps of zinc vacancies [15]. Although the related studies on CO gas sensors are diverse and have made major breakthroughs, much less attention has been focused on the theoretical calculation of CO gas sensors. In addition, the ZnGa₂O₄ layers are suitable as gas sensors, which can successfully detect CO, CO₂, SO₂, NO, and NO₂, and have wide bandgap of 5.2 eV, excellent optical characteristics, such as transparency in the near ultraviolet region, good conductivity, high resistance, as well as high thermal and chemical stability [1,14]. Accordingly, we have performed sufficient models to accurately predict CO gas adsorption on clean ZnGa₂O₄(111) and Pd-decorated ZnGa₂O₄(111) surfaces. Our analysis will focus on the work functions variation, adsorption energy, and the catalytic properties of palladium.

2. Computational Details

Systematic ab initio theoretical calculations were performed to study the equilibrium bond lengths, adsorption reactions, and work functions of carbon monoxide on the surfaces of the clean and Pd-decorated ZnGa₂O₄(111). The Vienna ab initio simulation package [16,17] was applied at the generalized gradient approximation (GGA) with the Perdew–Wang (PW91) correction [18,19] in all cases. The ground state structure of bulk ZnGa₂O₄ is cubic *Fd-3m* and performed using 8 Zn, 16 Ga, and 32 O atoms per unit cell, as shown in Figure 1. The Zn²⁺ and Ga³⁺ cations are distributed in tetrahedral and octahedral lattice sites, respectively. The cutoff energy and the self-consistent total energy criterion were set to 500 eV and 10^{−5} eV/unit cell, respectively, and the equilibrium lattice parameter of bulk ZnGa₂O₄ can be obtained as 8.334 Å. To simulate the work function of the clean and Pd-decorated ZnGa₂O₄(111) with and without adsorbed CO molecules, we have employed a repeated slab geometry with a 112-atom ZnGa₂O₄ with an in-plane lattice constants of 11.85 Å $\times$ 11.85 Å, which is sufficient to decouple the interactions between CO molecules, separated by a vacuum region equivalent to 20 Å vacuum, which decouples top and bottom interactions. Our slabs are terminated by the Ga–Zn–O surface with a low surface energy of 0.10 eV/Å², proposed earlier study by Jia et al. [20]. The top and side views for the selected adsorption sites of Ga–Zn–O-terminated ZnGa₂O₄(111) are displayed

in Figure 1. A gamma-centered $3 \times 3 \times 1$ Monkhorst–Pack grid was used for the density of state integration. This supercell was fully relaxed until the force acting on each atom was less than $0.001 \text{ eV}/\text{\AA}$.

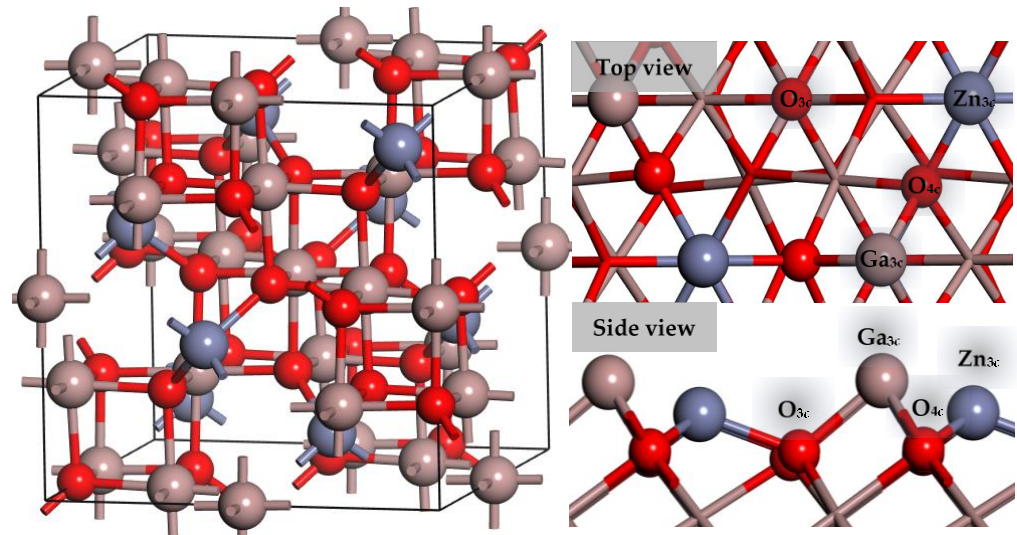


Figure 1. The bulk ZnGa_2O_4 crystal and top and side views of the $\text{ZnGa}_2\text{O}_4(111)$ surface. Surface atoms are labeled Ga_{3c} , Zn_{3c} , O_{3c} , and O_{4c} . Atoms are represented by spheres: Zn (gray, large), Ga (brown, medium-sized), and O (red, small).

To determine the preferred adsorption sites of the CO molecules on the $\text{ZnGa}_2\text{O}_4(111)$ surface, we labeled the surface atoms as Ga_{3c} , Zn_{3c} , O_{3c} , and O_{4c} in the top and side views of Figure 1. To gain further insight into the CO adsorption on the $\text{ZnGa}_2\text{O}_4(111)$ surface, we consider three following types. One type plotted in the upper panel of Figure 2 is that a carbon atom from a CO molecule perpendicular to the surface is adsorbed on Ga_{3c} , Zn_{3c} , O_{3c} , and O_{4c} sites, labeled as CO-C1, CO-C2, CO-C3, and CO-C4, respectively, or CO-C*i* denoted by model number *i* (where $i = 1-4$). The second type, plotted in the middle panel of Figure 2, is an oxygen atom from a CO molecule perpendicular to the surface is adsorbed on Ga_{3c} , Zn_{3c} , O_{3c} , and O_{4c} sites, labeled as CO-O1, CO-O2, CO-O3, and CO-O4, respectively, or CO-O*i* denoted by model number *i* (where $i = 1-4$). Thirdly, four adsorption models, CO-CO*i*, denoted by model number *i* (where $i = 1-4$), with both the O and C atoms from a CO molecule parallel to the surface interacting with the $\text{ZnGa}_2\text{O}_4(111)$ surface were constructed as shown in the bottom panel of Figure 2. In model CO-CO1 (CO-CO2), a carbon (an oxygen) atom from a CO molecule is adsorbed on the Ga_{3c} site. In model CO-CO3 (CO-CO4), a carbon (an oxygen) atom from a CO molecule is adsorbed on the Zn_{3c} site. On the other hand, we also constructed four adsorption models of Pd-decorated $\text{ZnGa}_2\text{O}_4(111)$, denoted as Pd-ZGO*i* (where $i = 1-4$), as shown in the upper panel of Figure 3. Here, the subscripts 1, 2, 3, and 4 in Pd-ZGO, respectively, indicate the positions of the initial adsorbed sites Ga_{3c} , Zn_{3c} , O_{3c} , and O_{4c} on the $\text{ZnGa}_2\text{O}_4(111)$ surface. An oxygen atom from a CO molecule perpendicular to the surface is adsorbed on Pd-ZGO*i* models, labeled as CO-Pd-ZGO*i* (where $i = 1-4$), as shown in the bottom panel of Figure 3. The initial distance from the adsorbed atom to the surface atom was set as the sum of the van der Waals radii of each of atom.

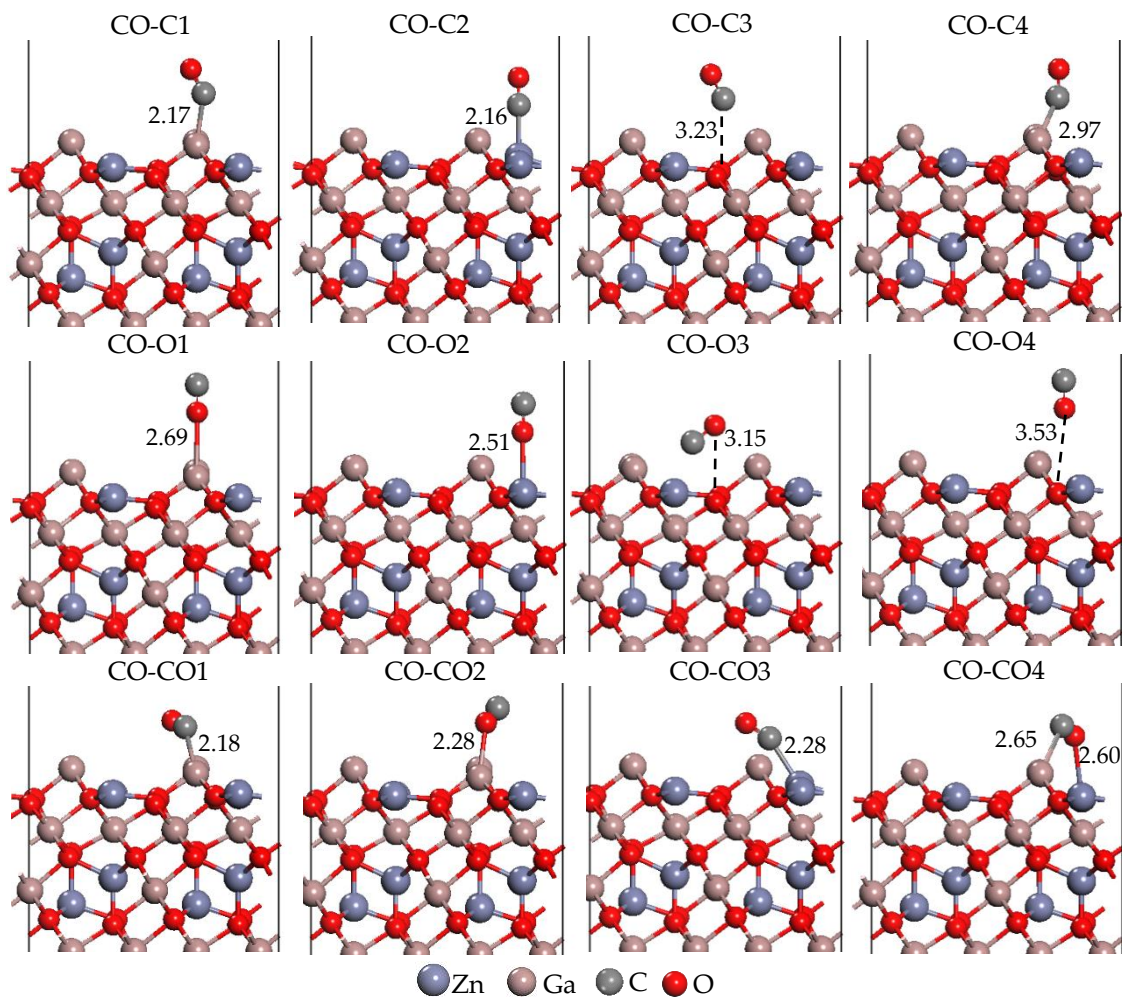


Figure 2. Ball and stick structural representations of the optimized CO-Ci, CO-Oi and CO-COi considered in this study. Atoms are represented by spheres: Zn (gray, large), Ga (brown, large), C (gray, medium-sized), and O (red, small). Bond lengths are given in Å.

The adsorption of gas molecules on the surface of the $\text{ZnGa}_2\text{O}_4(111)$ surface causes a change in the work function $\Delta\Phi$, resulting in a change between the resistance in the presence of the investigated gas (R_g) and the resistance in the reference gas (R_a) to measure the gas sensitivity. The gas sensitivity could be determined from the ratio of R_g/R_a , and the work function change $\Delta\Phi$ is given by [3]

$$\Delta\Phi = \Delta X + kT \ln(R_g/R_a) \quad (1)$$

where ΔX denotes the change in electron affinity and kT denotes the product of the Boltzmann constant k and the temperature T . Note that the work function Φ is given by the following equation [21]:

$$\Phi = E_{\text{VAC}} - E_F \quad (2)$$

where E_{VAC} and E_F are the energies of a vacuum level and a Fermi level, respectively. Electrons in solids and molecules obey the Fermi–Dirac distribution. Electrons with the same quantum properties are forbidden to occupy the same energy state, while up to two electrons with opposite spins are allowed to occupy one energy state. The energy of the highest occupied state is known as the Fermi energy. Additionally, the limitations of the first-principles calculations do not allow the calculation of the absolute vacuum level because it depends on the periodic boundary conditions and surface terminations of the materials. The vacuum level here refers to the energy estimated from the planar average of

the potential of the periodic slabs in the vacuum region along the direction perpendicular to the surface of the $\text{ZnGa}_2\text{O}_4(111)$ surface. The gas adsorption on the $\text{ZnGa}_2\text{O}_4(111)$ surface that enables exothermic or endothermic reaction is also one of the serious issues affecting the sensitivity of the sensor. The adsorption energy ΔE can be calculated through the equation:

$$\Delta E = E_{\text{ZGO-CO}} - (E_{\text{ZGO}} + E_{\text{CO}}) \quad (3)$$

where $E_{\text{ZGO-CO}}$ is the total energy of a target molecule or a CO molecule adsorbed on the $\text{ZnGa}_2\text{O}_4(111)$ surface, and E_{ZGO} and E_{CO} are the total energies of a slab of $\text{ZnGa}_2\text{O}_4(111)$ surface model and a free (isolated) CO molecule, respectively. Whether the adsorption energy is related to the work function is also an issue to be discussed in this study.

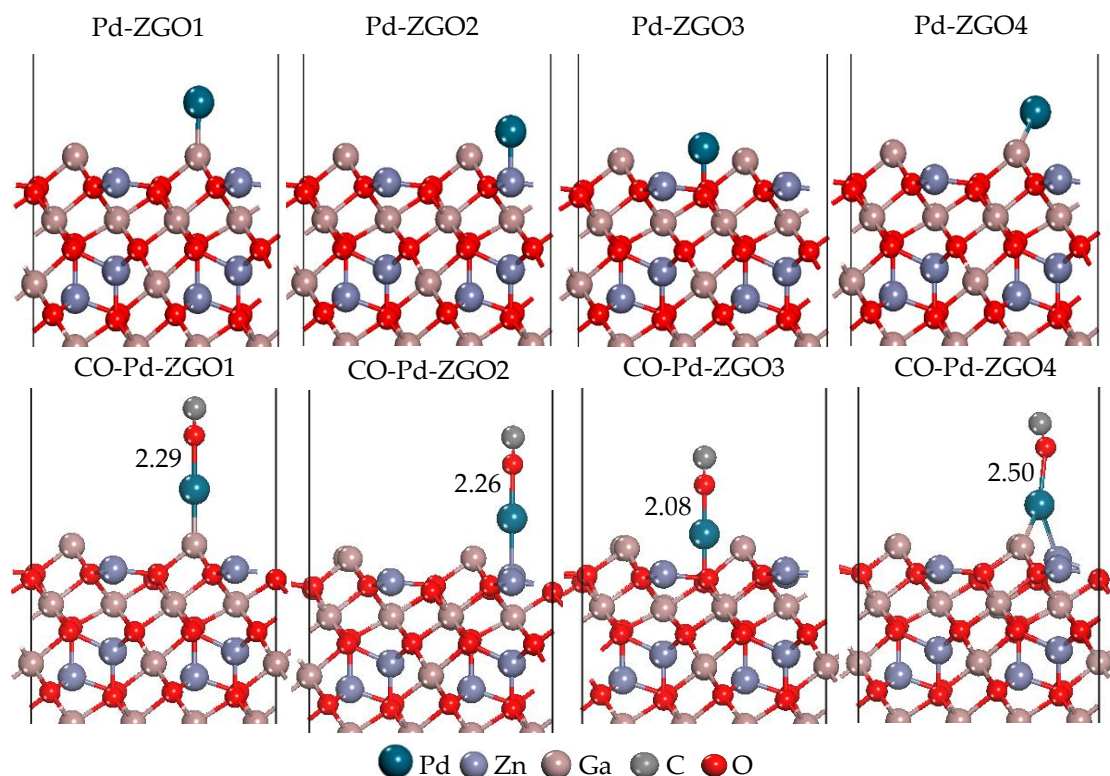


Figure 3. Ball and stick structural representations of the optimized Pd-ZGO $_i$ and CO-Pd-ZGO $_i$ considered in this study. Atoms are represented by spheres: Pd (dark green, very large), Zn (gray, large), Ga (brown, large), C (gray, medium-sized), and O (red, small). Bond lengths are given in Å.

3. Results and Discussion

Calculated equilibrium bond lengths (Å) for the CO-C $_i$, CO-O $_i$, CO-CO $_i$, Pd-ZGO $_i$, and CO-Pd-ZGO $_i$ are shown in Figures 2 and 3. In models CO-C $_i$ and CO-O $_i$, the equilibrium bond lengths are ranged from 2.16 Å to 3.53 Å. The lowest bond length occurs in the CO-C2, where the carbon atom of a CO molecule perpendicular to the surface is bonded to the zinc atom. The bond length of the CO-C $_i$ is smaller than the CO-O $_i$ for each model number i . The smallest bond length of model CO-O $_i$ is 2.51 Å. In models CO-CO $_i$, the bond lengths are ranged from 2.18 Å to 2.65 Å. The equilibrium bond lengths for models CO-CO $_i$ are remarkably similar to those of the CO-C $_i$ and CO-O $_i$. For example, the equilibrium bond length for the CO-C1 is 2.17 Å, where the carbon atom of a CO molecule is bonded to the Ga atom of the $\text{ZnGa}_2\text{O}_4(111)$ surface. Similarly, the bond length for the CO-CO1 is 2.18 Å, showing the adsorption of CO molecule from being parallel to the surface to being perpendicular to the surface. In the case of the CO-CO4, our calculations show that the corresponding bond length for C-Ga and O-Zn bonds are 2.65 Å and 2.60 Å, respectively, suggesting that an increased bond length means less attraction between atoms. In our

preliminary work [5], a Pd atom on the $\text{ZnGa}_2\text{O}_4(111)$ surface shows that the calculated Pd-Ga, Pd-Zn, and Pd-O equilibrium bond lengths are 2.32 Å, 2.57 Å, and 2.04 Å for Pd-ZGO1, Pd-ZGO2, and Pd-ZGO3, respectively. In contrast with the Pd atoms adsorbed on the $\text{ZnGa}_2\text{O}_4(111)$ surface, the calculated equilibrium O-Pd bond lengths for models CO-Pd-ZGO i are between 2.08 Å and 2.50 Å.

The adsorption energies ΔE of a CO molecule on the $\text{ZnGa}_2\text{O}_4(111)$ surface without Pd atoms are shown in Table 1. The calculated adsorption energies ranged from -0.04 eV to -1.88 eV, indicating that all adsorption reactions occurred spontaneously. Note that spontaneous reactions occur in the direction of decreasing Gibbs free energy change ΔG . The Gibbs free energy change consists of the change in enthalpy, ΔH , and the change in entropy, ΔS , with the following formula: $\Delta G = \Delta H - T\Delta S$. The enthalpy change is defined as the sum of the change in internal energy, ΔE , and the product of the pressure, P , and the change in volume, ΔV , as follows: $\Delta H = \Delta E + P\Delta V$. Therefore, the Gibbs free energy change can be expressed as: $\Delta G = \Delta E + P\Delta V - T\Delta S$. In our study, we ignored the contribution of entropy changes and the volume changes in the ZnGa_2O_4 structure. The Gibbs free energy change can be further simplified to the internal energy change caused by the kinetic, potential, and chemical energy of the material system. Negative Gibbs free energy change, negative internal energy change, or negative adsorption energy ΔE provides a means by which spontaneous physical and chemical changes can occur without any external help. Conversely, positive adsorption energies suggest that the corresponding endothermic process can be supported by increasing the temperature. It can be clearly seen that the CO-C1 has the lowest adsorption energy of -1.88 eV. Consistently, this adsorption site Ga_{3c} exists a low C-Ga bond length of 2.17 Å, i.e., a strong interaction, suggesting that the Ga_{3c} site is more favored if CO molecules are adsorbed on the $\text{ZnGa}_2\text{O}_4(111)$ surface. It is therefore also of significant interest to carry out a detailed comparison of the adsorption energies of the CO-O i with those obtained from the CO-C i . The CO-O i have low adsorption energies, and ranged from -0.04 eV to -0.44 eV, showing less attraction between atoms. It is perhaps not surprising that the CO-O i have longer bond lengths than the CO-C i . In the cases of the CO-CO i , the CO-CO2 has the lowest adsorption energy of -1.55 eV and the CO-CO1 exhibits the second lowest adsorption energy of -1.28 eV. The oxygen atoms of CO molecules are more attractive to the Ga surface atoms of the $\text{ZnGa}_2\text{O}_4(111)$ surface than the carbon atoms of CO molecules.

The gas sensing sensitivity of the various CO-C i , CO-O i , CO-CO i , and CO-Pd-ZGO i configurations is intimately related to their surface resistances or work function changes. A common approach adopted in many studies is to analyze energies of the Fermi level and the vacuum level to determinate their work functions. We use the clean $\text{ZnGa}_2\text{O}_4(111)$ surface as a reference state surface to calculate the work function of 3.91 eV, as shown in Table 1. In Table 1, it can be clearly seen that the Fermi energies of all models increase when a CO molecule is adsorbed on the $\text{ZnGa}_2\text{O}_4(111)$ surface. This is because a CO molecule adds extra electrons to the system, causing the increase of the Fermi energy. From Table 1, it is apparent that the vacuum energies of the only two models, i.e., the CO-C1 and CO-O1, are lower than the reference value (0.41 eV) of the vacuum level of the clean $\text{ZnGa}_2\text{O}_4(111)$, leading to the small work functions. However, it is interesting to note that the bonding of carbon or oxygen atoms from CO molecules to Ga surface atoms on the $\text{ZnGa}_2\text{O}_4(111)$ surface decreases the vacuum energy level, which may explain why the Ga_{3c} sites of adsorbed gas molecules have a great influence on the gas sensitivity. In the CO-C i , the work function is proportional to the adsorption energy, while the CO-C1 model had the largest reduction with the work function change of -0.53 eV. In the CO-O i , CO-O1 has the largest reduction with the work function change of -0.55 eV. Surprisingly, the work function change of CO-O1 is slightly higher than that of CO-C1 (-0.53 eV), which means that the Ga_{3c} sites of adsorbed CO molecules have a great influence on the gas sensitivity. In the CO-CO i , CO-CO2 has the largest reduction with the work function change of -0.49 eV, showing the oxygen atoms of CO molecules are more sensitive to the Ga surface atoms of

the $\text{ZnGa}_2\text{O}_4(111)$ surface than the carbon atoms of CO molecules, corresponding to the work function change of -0.43 eV.

Table 1. Calculated vacuum energy E_{VAC} , Fermi energy E_F , work function with CO molecules $\Phi_{\text{S, CO}}$, and without CO molecules Φ_{S} , work function changes $\Delta\Phi$, and adsorption energy ΔE of $\text{ZnGa}_2\text{O}_4(111)$, CO-Ci, CO-Oi, CO-COi, Pd-ZGOi, and CO-Pd-ZGOi. All energies are presented in eV.

Models	E_{VAC} (eV)	E_F (eV)	$\Phi_{\text{S, CO}}$ (eV)	Φ_{S} (eV)	$\Delta\Phi$ (eV)	ΔE (eV)
$\text{ZnGa}_2\text{O}_4(111)$	0.41	-3.50	-	3.91	-	-
CO-C1	0.23	-3.15	3.38	-	-0.53	-1.88
CO-C2	0.51	-3.28	3.79	-	-0.11	-0.68
CO-C3	0.63	-3.37	4.00	-	0.09	-0.17
CO-C4	0.49	-3.23	3.72	-	-0.18	-0.70
CO-O1	0.16	-3.20	3.36	-	-0.55	-0.44
CO-O2	0.53	-3.24	3.77	-	-0.13	-0.25
CO-O3	0.69	-3.29	3.98	-	0.07	-0.04
CO-O4	0.58	-3.26	3.84	-	-0.07	-0.21
CO-CO1	0.42	-3.06	3.48	-	-0.43	-1.28
CO-CO2	0.21	-3.21	3.42	-	-0.49	-1.55
CO-CO3	0.24	-3.41	3.65	-	-0.26	-0.15
CO-CO4	0.34	-3.47	3.81	-	-0.09	-0.17
Pd-ZGO1	0.65	-3.00	-	3.65	-	-
Pd-ZGO2	0.76	-3.08	-	3.84	-	-
Pd-ZGO3	0.65	-3.29	-	3.94	-	-
Pd-ZGO4	0.67	-3.08	-	3.75	-	-
CO-Pd-ZGO1	-0.30	-3.16	2.86	-	-0.79	-1.58
CO-Pd-ZGO2	0.20	-2.96	3.16	-	-0.68	-3.36
CO-Pd-ZGO3	-0.02	-3.21	3.19	-	-0.75	-2.78
CO-Pd-ZGO4	0.40	-2.92	3.32	-	-0.43	-2.80

Based on our previous study [5], we found that Pd atoms can be used to enhance the performance of ZnGa_2O_4 -based gas sensors for detecting NO_2 and H_2S . Here, we calculate the work function change and adsorption energy of the CO-Pd-ZGOi by following a similar procedure, as listed in Table 1. The work function changes of the CO-Pd-ZGOi range from -0.43 to -0.79 eV, making the latter 1.43 times larger than the former. Our results show that an increase in the work function changes can be used to improve the performance of the gas sensor. In addition, the adsorption energies of CO-Pd-ZGOi drop drastically and range from -1.58 to -3.36 eV, indicating CO molecules are catalyzed by Pd atoms to promote adsorption on the surface of $\text{ZnGa}_2\text{O}_4(111)$ to enhance the work function change. In the CO-Pd-ZGOi, CO-Pd-ZGO2 has the lowest adsorption energy of -3.36 eV. This implies that the existence of the Pd atom on the initial adsorbed site Zn_{3c} of the $\text{ZnGa}_2\text{O}_4(111)$ surface is particularly attractive for CO molecules.

4. Conclusions

The adsorption energy and work function change of CO on the $\text{ZnGa}_2\text{O}_4(111)$ surface have been investigated using first-principles calculations. Our results show that a single CO molecule on clean and Pd-doped $\text{ZnGa}_2\text{O}_4(111)$ surfaces exhibit maximum work function changes of -0.55 eV and -0.79 eV, respectively, indicating Pd-doped ZnGa_2O_4 -based gas sensors can improve sensitivity to detect CO molecules. The adsorption energies for a single CO molecule on the clean and Pd-doped $\text{ZnGa}_2\text{O}_4(111)$ surface have the lowest adsorption energy of -1.88 eV and -3.36 eV, respectively, which means that CO molecules are catalyzed by Pd atoms to promote adsorption on the surface of $\text{ZnGa}_2\text{O}_4(111)$ to

enhance the work function change. This result also leads that the adsorption energy of CO molecules is positively correlated with the sensitivity or the work function change of CO on the $\text{ZnGa}_2\text{O}_4(111)$ surface. Our calculations for work function change for gas sensor applications overcome many issues encountered in potential energy barrier for electrons caused by gas adsorption on the ZnGa_2O_4 surface and offers promising applications in next-generation sensing technologies, including not only adsorption energy indicating a spontaneous reaction progression, but also designing high-performance single-atom catalysts (SACs), such as the recently demonstrated catalytic CO oxidation on MgAl_2O_4 -supported iridium single atoms [22].

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