

ELECTRONIC PROPERTIES OF SINGLE-LAYER GERMANENE SURFACES WITH GAS ADSORPTION

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Abstract. The calculations of two - dimensional material structure of germanene and the adsorption of gas molecules (such as CO, CO₂, N₂) on germanene are performed by using density functional theory. The results show that germanene has zero-band gap energy and non-spin polarized characteristics. The adsorption of gas molecules on the surface of germanene plays a role in the tunable band gap. The adsorption energy of CO is lower than that of CO₂ and N₂, indicating that CO is more easily to be absorbed by the other two gases. This result makes germanene a potential candidate for CO adsorption devices, contributing to the reduction of the amount of CO in the air to create a clean beautiful environment.

Keywords: Germanene, gas adsorption, DFT.

1. Introduction

Two-dimensional materials have been interested after Geim and Novoselov [1] discovered graphene from graphite, which brought a special interest to the scientists prompting them to exclaim "For the first time in the history of science, humans have been able to see, touch, and use a material that is as thin as the thickness of an atom" [2]. Low - dimensional materials are predicted to have many advantages compared to previous materials.

Since the successful identification of graphene from mechanically exfoliated graphite and the subsequent discovery of unusual properties [3] graphene has attracted vast experimental and theoretical attention [4, 5]. However, the physisorption of common gas molecules on pristine graphene limits its immediate potential [6]. Silicene and germanene are two-dimensional allotropes of silicon and germanium analogies of graphene. Recently, silicene and germanene, the two-dimensional allotrope of silicon and germanium analogues to graphene, have also attracted increasing attention. In experiments, silicene was successfully grown on Ag [7-10] Ir₁₃ and ZrB₂₁₄ substrates. Most recently, germanene was also successfully grown on Pt(111) [11] Germanene, multilayer hydrogen-terminated

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germanene, has also been synthesized and then mechanically exfoliated to a single layer onto SiO₂/Si surface [12]. Silicene and germanene show the most outstanding properties similar to those of graphene such as quantum hall effect [13], ferromagnetism [14], high carrier mobility [15], half-metallic [16], and a topological insulator [17]. Several researches are now directed at the germanene crystal [18], a material synthesized on platinum substrates [13] and gold [19].

Germanene is predicted to have great strength, conductivity, and surface tension. However, the zero-gap properties of germanene make them very difficult to apply in nature. Therefore, opening a sizable band gap in them without heavy loss of carrier mobility is one of the key issues in present research on them [20]. Additionally, the germanene lattice offers the possibility to open a band gap via for instance an externally applied electrical field, adsorption of foreign atoms, or coupling with a substrate [21].

In particular, the germanene surface can absorb gas molecules [22] that is helpful in the application of sensors or purified devices. Therefore, germanene has recently been one of the topics that physicists are increasingly interested in. Finding a material that has many advantages over previous materials will create a new leap for material science. Currently, the amount of gas CO and CO₂ is becoming more and more in the air. If we can find a material whose surface can absorb a significant amount of these toxic gases, it will contribute to purifying the air.

2. Content

2.1. Computational details

It is almost impossible to solve exactly the Schrodinger equation. By using density functional theory (DFT) [23, 24] with some approximations (local density approximation-LDA or generalized gradient approximation-GGA), the Schrödinger equations for any systems, especially for multi-particle systems can be solved. Our study performs the DFT calculations that are implemented in software package CASTEP (originally from Cambridge Serial Total Energy Package) [25]. The plane-wave basis set is employed for the valence electron wave function with cut-off energy of 450 eV. For the exchange-correlation energy, the LDA was employed within the Perdew-Burke-Ernzerhof (PBE) functional [26, 27]. Monkhorst-Pack k-point grids [28] showed total energy convergence within 1 meV per atom. Structural relaxation was terminated when the maximum Hellman-Feynman forces acting on each atom in the unit cell dropped to 0.001 eV/Å. The vacuum space in the Z direction is about 20 Å to separate the interactions between the neighboring slabs. For a 4×4 supercell, 5×5×1 k-points in Brillouin zone are sampled for geometry optimization and 9×9×1 k-points for static calculation in order to obtain accurate total energies and electronic densities of states.

2.2. Results and discussions

2.2.1. Pure germanene

** Convergence calculation*

The geometry structure of the Germanene surface is shown in Figure 1.

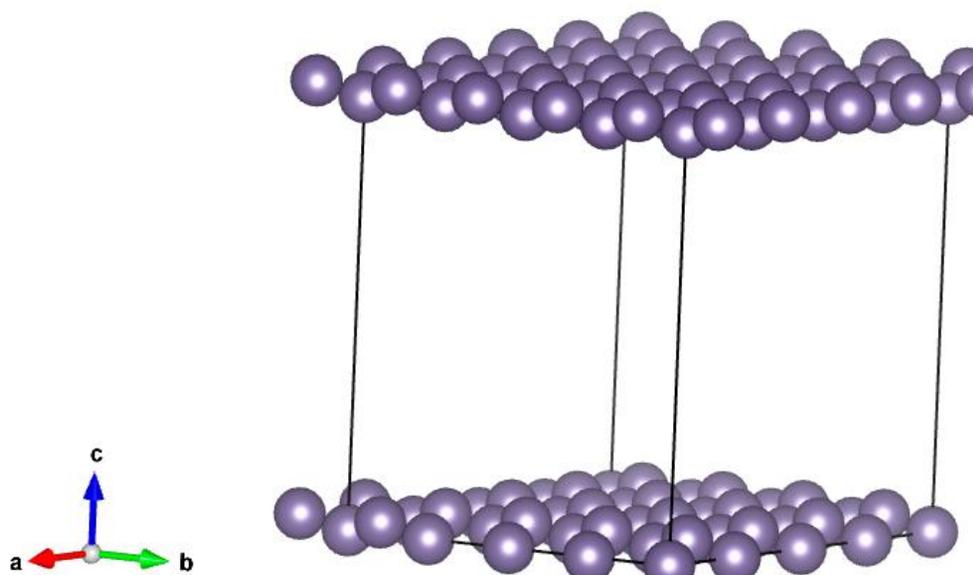


Figure 1. Geometry structure of Germanene surface

Analysis of utilizing two calculation functions LDA and GGA before optimizing the geometric structures is performed and selected by comparing the total energy of germanene. The obtained results are shown in Table 1.

Table 1. The total energies of Germanene when different approximations are applied

Function	E (eV)
LDA	-2533.9287
GGA+PBE	-2532.9473
GGA+RPBE	-2533.4758
GGA+PW91	-2532.9473
GGA+WC	-2532.7329
GGA+PBESOL	-2531.5737

From Table 1, the lowest energy value is obtained when using LDA, corresponding to the most stable configuration. Therefore, in the calculation process of this study, the LDA function is selected.

*** Cutoff energy (ENCUT) and k-point**

An essential condition in the calculation process is ENCUT value and k-point suitable for the material. It helps reduce the computational cost. Investigating the convergence of energy according to values, ENCUT was chosen at the point where the energy began to be converged. The ENCUT value varies from 250 eV to 530 eV with a

jump of 20 and the total energy values of the system correspond to those of Cutoff energy. The obtained energy values are plotted in Figure 2.

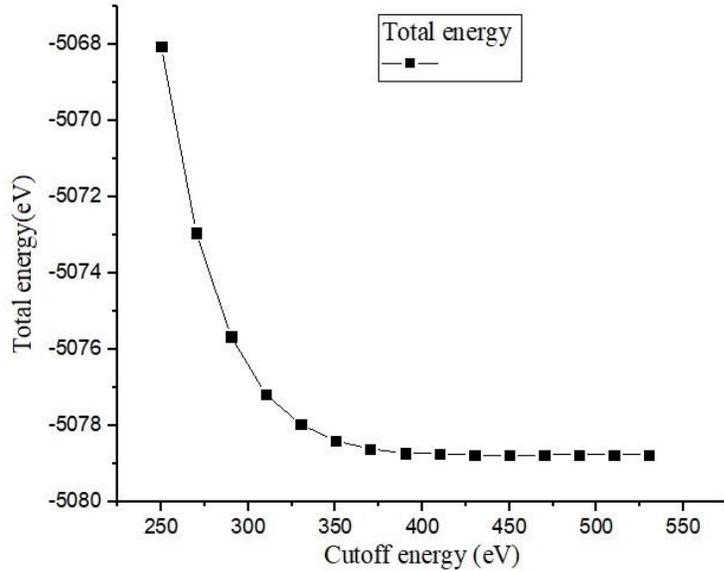


Figure 2. The dependence of the total energy on Cutoff energy

The energy begins to converge at the ENCUT point is 450 eV. Therefore, the Cutoff energy value chosen for the calculation is 450 eV. Next, the ENCUT is fixed and the k-point grid is varied in order to consider the convergence of total energy. The obtained values are shown in Figure 3.

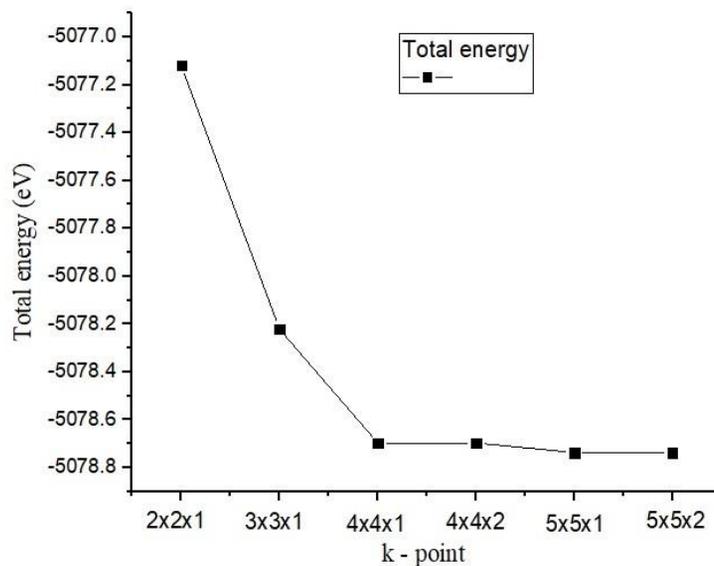


Figure 3. The dependence of the total energy on k-point grid

The energy starts to converge at the k-point $5 \times 5 \times 1$. So $5 \times 5 \times 1$ is the k-point and fixed for the next calculation. The optimization is performed where the obtained cut-off energy and the k-point grid values are applied. The optimized lattice parameters are shown in Table 2.

Table 2. The optimized lattice parameters of germanene

a (Å)	b (Å)	c (Å)
4.13084	4.13084	20.49017

This obtained optimized structure is then utilized in order to investigate the electronic properties as shown in the following sections.

*** Band structure and density of states**

The calculated electronic band structure and the total density of states (TDOS) of pure germanene shown in Figures 4 and 5 reveal that germanene is a zero-gap semiconductor. The zero-gap properties of germanene make it very difficult to employ in the real application when applying in electronic devices such as high-performance field-effect transistors (FETs) operating at room temperature. Therefore, opening a sizable band gap is one of the key issues in the present research on this material.

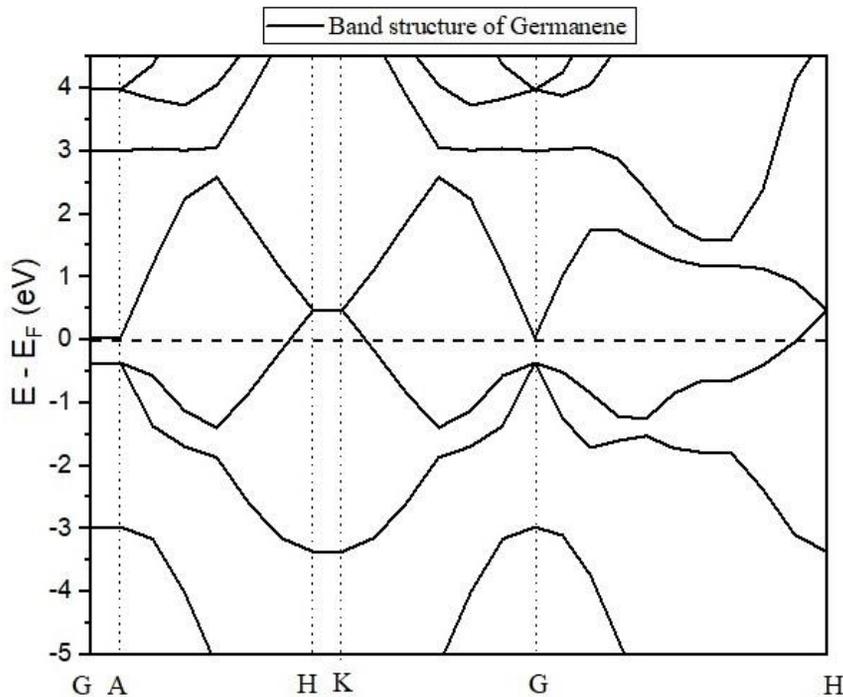


Figure 4. Electronic band structures of germanene. $A(0, 0, 1/2)$, $H(1/3, 1/3, 1/2)$, $K(1/3, 1/3, 0)$ and $G(0, 0, 0)$ are some high symmetry points in the first Brillouin zone. The Fermi level of germanene is set to zero and represented by the dashed horizontal line

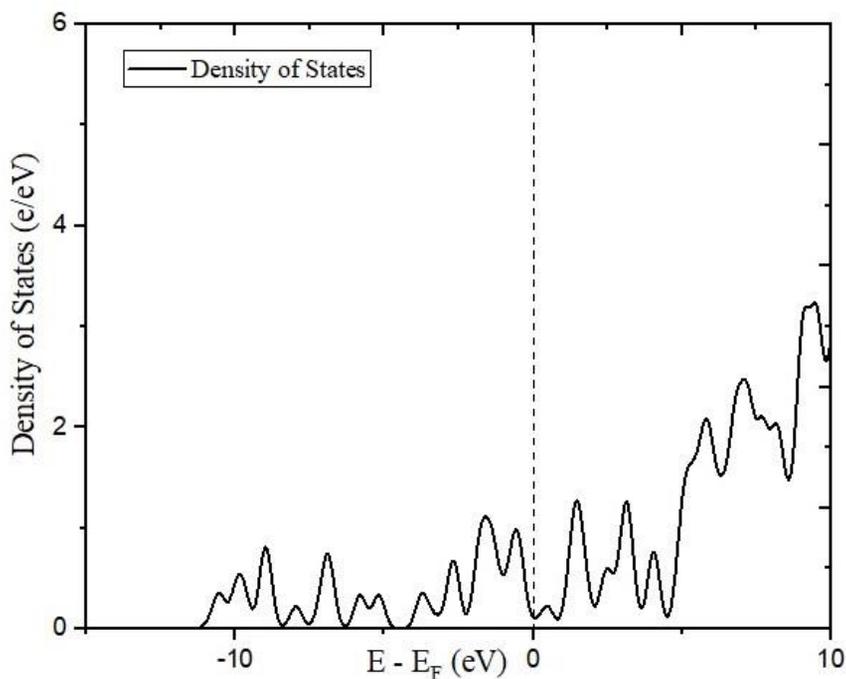


Figure 5. The total density of states of germanene. The Fermi level of germanene is set to zero and represented by the dashed vertical line

2.2.2. Gas adsorption

* Adsorption energy

To evaluate the stability of the adsorption of gas molecules on germanene, the adsorption energy is defined as [22]

$$E_a = E_{Ge-X} - E_{Ge} - E_X \quad (1)$$

where E_a is the adsorption energy, E_{Ge-X} is the total energy of germanene with gas molecules adsorption, E_{Ge} is the total energy of pure germanene and E_X is the total energy of gas molecules. The adsorption energy values are calculated for CO, CO₂ and N₂ gas adsorbed on the germanene surface and listed in Table 3.

Table 3. Energy, band gap and energy adsorption

Gas molecules	d_{Ge-X} (Å)	Total energy (eV)	Band gap (eV)	E_a (eV)
CO	3.35	-5673.4657	0.419	-0.1573
CO ₂	3.40	-6112.2220	0.407	-0.0620
N ₂	3.54	-5630.8736	0.411	-0.0095

It can be seen from Table 3 that the adsorption energies for three gas molecules adsorption CO, CO₂, and N₂ are all negative. Therefore, germanene is also chemically inert to these gas molecules, similar to graphene and silicene. From the calculation results listed in Table 3, the adsorption energy is lowest for CO molecules adsorption, followed by CO₂ and N₂ adsorption. Among these three adsorbents, the most stable adsorption configuration for the adsorption of gas molecules on germanene is found for CO gas molecules. Since CO molecules are easily absorbed onto the surface of germanene than CO₂ and N₂ molecules, germanene can be applied to design devices that on the surface can adsorb CO, helping to reduce the lack of toxic gases in the air, contributing to a beautifully clean environment.

*** Electronics properties of Germanene when gas adsorbed**

To analyze the effect of the adsorbed molecules on the electronic structures of germanene, the electronic band structures are calculated and plotted in Figure 6. Sizable band gaps of (407 - 419 meV) are opened at the Dirac point of germanene for all the adsorption of CO₂, N₂, and CO on germanene.

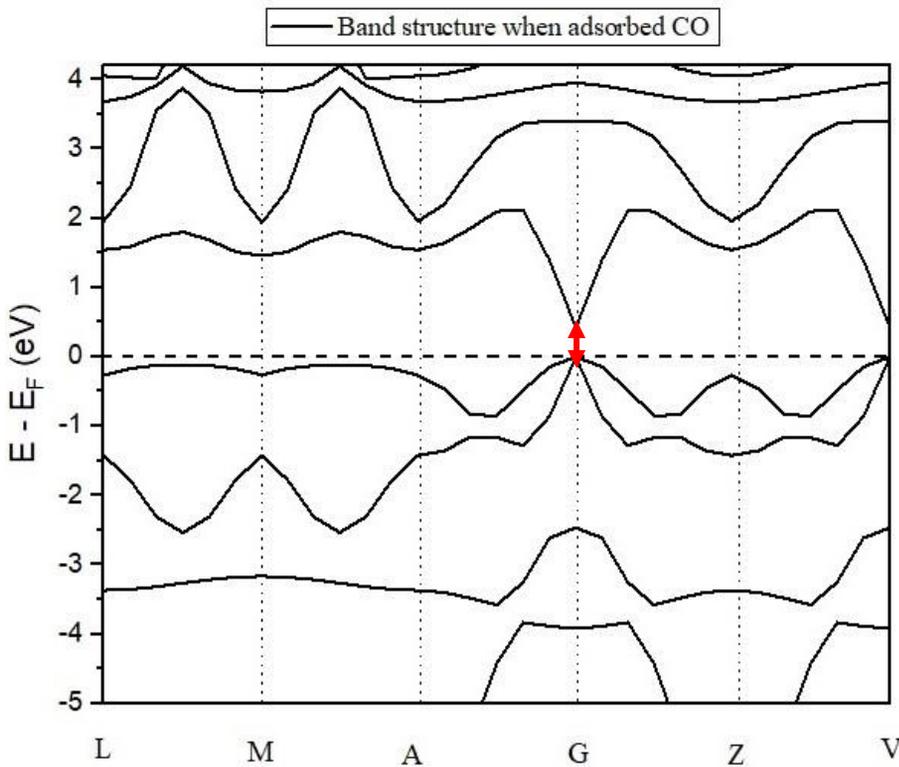


Figure 6a. Band structure of germanene adsorbed with CO

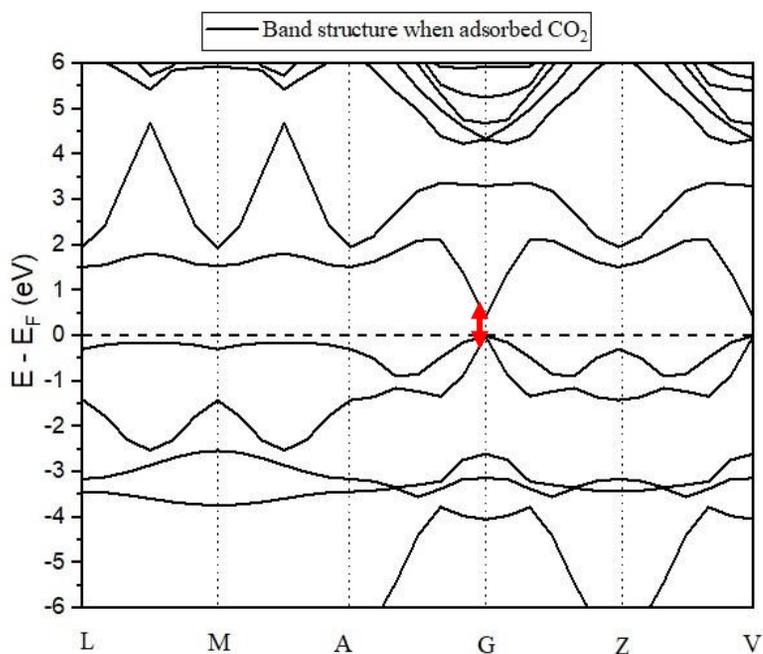


Figure 6b. Band structures of germanene adsorbed with CO₂

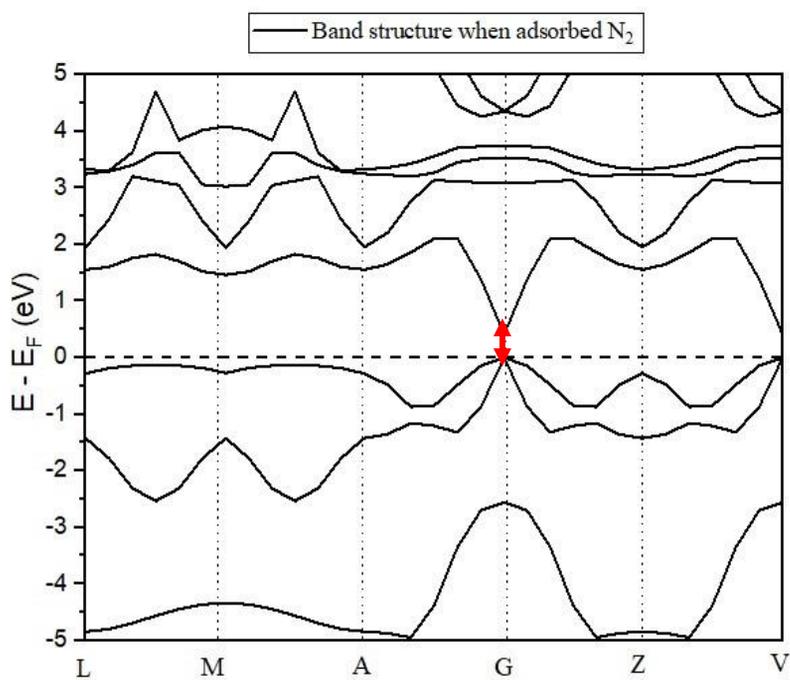


Figure 6c. Band structures of germanene adsorbed with N₂

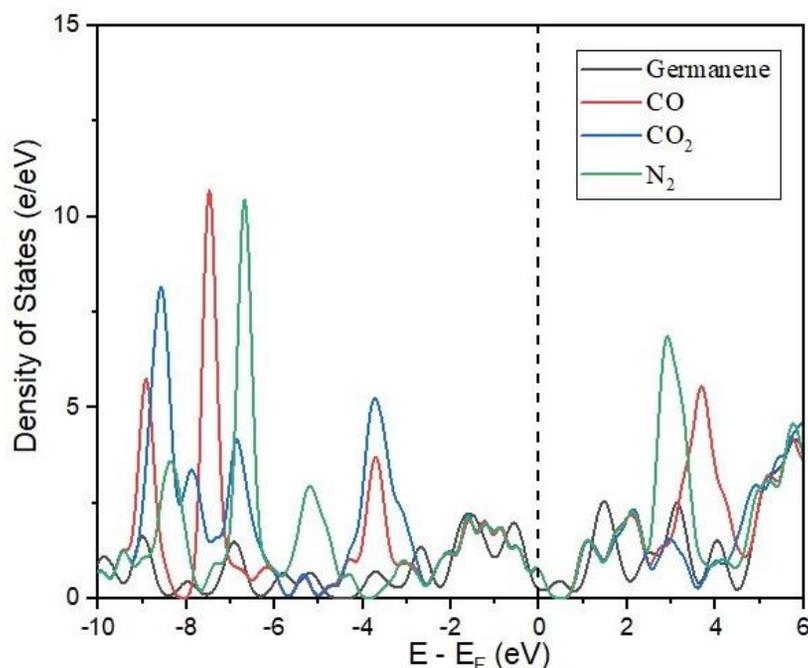


Figure 7. Total Density of States of germanene when gas molecules adsorbed

Here, the origin of gas molecules' adsorption on germanene is investigated by analyzing the TDOSs plotted in Figure 7. The TDOSs show that the frontier orbitals (highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO)) of CO, CO₂ and N₂ are close to the Dirac point (or the Fermi level) of germanene. Thus, these gas molecules have higher reactivity to germanene.

3. Conclusions

In conclusion, we investigate the adsorption of CO, CO₂, and N₂ molecules on germanene on the basis of density functional theory calculations. We find that the pure germanene has zero band gap energy and does not have spin polarization. The tunable band gap of germanene can be observed through the adsorption of gases to the surface. The most stable structure is found for CO adsorption on the surface of germanene with the lowest adsorption energy. This makes germanene a potential candidate for devices to adsorb the existence of CO in the environment, contributing to the reduction of toxic gases in the air and environment protection.

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